L Number	Hits	Search Text	DB	Time stamp
1	541597	circular dichroism	USPAT	2003/07/22 17:08
2	20782	chiral	USPAT	2003/07/22 17:07
3	259	(circular dichroism) same chiral	USPAT	2003/07/22 17:07
4	1014896	absolute configuration	USPAT	2003/07/22 17:09
5	28	((circular dichroism) same chiral) same (absolute configuration)	USPAT	2003/07/22 17:08
6	1524	circular near dichroism	USPAT	2003/07/22 17:09
7	3446	absolute near configuration	USPAT	2003/07/22 17:09
8	23	(circular near dichroism) same (absolute near configuration)	USPAT	2003/07/22 17:12
9	6163	chromophore	USPAT	2003/07/22 17:47
10	15	(circular near dichroism) and (absolute near configuration) and chromophore	USPAT	2003/07/22 17:57
11	3857	fixing near agent	USPAT	2003/07/22 17:58
12	0	(circular near dichroism) same (fixing near agent)	USPAT	2003/07/22 17:58
13	0	(circular near dichroism) and (fixing near agent)	USPAT	2003/07/22 17:59
14	2	cirular near dichroism	USPAT; US-PGPUB; DERWENT	2003/07/22 18:00
18	2216	circular near dichroism	USPAT; US-PGPUB; DERWENT	2003/07/22 18:00
22	6405	fixing near agent	USPAT; US-PGPUB; DERWENT	2003/07/22 18:00
26	2	(circular near dichroism) and (fixing near agent)	USPAT; US-PGPUB; DERWENT	2003/07/22 18:02
30	173989	cd	USPAT; US-PGPUB; DERWENT	2003/07/22 18:02
34	23	cd same (fixing near agent)	USPAT; US-PGPUB; DERWENT	2003/07/22 18:02

EAST - [default.wsp:1]

File View Edit Tools Window Help

- Drafts
- Pending
- Active
  - L1: (0) diphenic near monoester
  - L2: (705) diphenic
  - L3: (7584) monoester
  - L4: (4) l2 same l3
  - L5: (3655) diphenyl same carboxylic
  - L6: (7584) monoester
  - L7: (10) l5 same l6
  - L8: (402) diphenyl near dicarboxylic
  - L9: (0) l8 near l6
  - L10: (0) l8 near monomethy
  - L11: (2) l8 near ester
  - L12: (86) l8 same ester
  - L13: (7) l8 same monoester
  - L14: (0) achiral near chromophore
  - L15: (3) achiral same chromophore
- Failed
- Saved
- Favorites
- Tagged (0)
- UDC
- Queue
- Trash

Search | Visb | Browse | Queue | Clear

DBs USPAT | Plurals

Default operator: OR | Highlight all hit terms initially

achiral same chromophore

BRS f... | IS&R ... | Image | Text | HTML

	U	1	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	R
1	☐	☐	US 6569504 B1	20030527	57	Mesogenic materials with anomalous birefringence dispersion and high	428/1.1	252/299.01; 252/299.2;	
2	☐	☐	US 6139771 A	20001031	55	Mesogenic materials with anomalous birefringence dispersion and high	252/299.01	252/299.2; 252/299.6;	
3	☐	☐	US 5011756 A	19910430	6	Storage of optical information using photochiroptical effect	430/19	346/135.1; 349/98;	

Hits | Details | HTML

Ready NUM

10082251

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(FILE 'HOME' ENTERED AT 14:11:24 ON 22 JUL 2003)

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L3 182 S L1 SSS FULL

FILE 'CAPLUS' ENTERED AT 14:13:55 ON 22 JUL 2003
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L5 209 S L4 NOT DIPHENIC
L6 532 S BIPHENYL (P) DICARBOXYLIC
L7 163 S L5 NOT L6
L8 47 S L7 AND PATENT/DT
L9 2 S L7 AND ACHIRAL
L10 413 S 482-05-3/RN
L11 76 S L7 NOT L10
L12 75 S L11 NOT L9
L13 27 S L12 AND PATENT/DT

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L16 144 S L14 SSS FULL SUB=L3

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L21 59 S L20 NOT L9
L22 27 S L21 AND PATENT/DT
L23 1 S L19 AND ACHIRAL
L24 0 S L23 NOT L9
L25 0 S L22 NOT L13
L26 39 S L4 NOT L17
L27 38 S L26 NOT L9
L28 38 S L27 NOT L13
L29 3 S L28 AND PATENT/DT
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L31 1 S L30 AND CD
L32 34 S L30 NOT L31
L33 32 S L32 NOT 6926-84-7P/RN

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10082251

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L3           182 S L1 SSS FULL

     FILE 'CAPLUS' ENTERED AT 14:13:55 ON 22 JUL 2003
L4           560 S L3
L5           209 S L4 NOT DIPHENIC
L6           532 S BIPHENYL (P) DICARBOXYLIC
L7           163 S L5 NOT L6
L8            47 S L7 AND PATENT/DT
L9             2 S L7 AND ACHIRAL
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L13           27 S L12 AND PATENT/DT

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L18          192 S L17 NOT DIPHENIC
L19          146 S L18 NOT L6
L20           59 S L19 NOT L10
L21           59 S L20 NOT L9
L22           27 S L21 AND PATENT/DT
L23            1 S L19 AND ACHIRAL
L24            0 S L23 NOT L9
L25            0 S L22 NOT L13
L26           39 S L4 NOT L17
L27           38 S L26 NOT L9
L28           38 S L27 NOT L13
L29            3 S L28 AND PATENT/DT
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10082251

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L32          34 S L30 NOT L31
L33          32 S L32 NOT 6926-84-7P/RN
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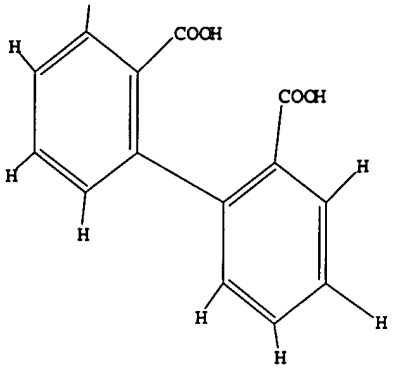

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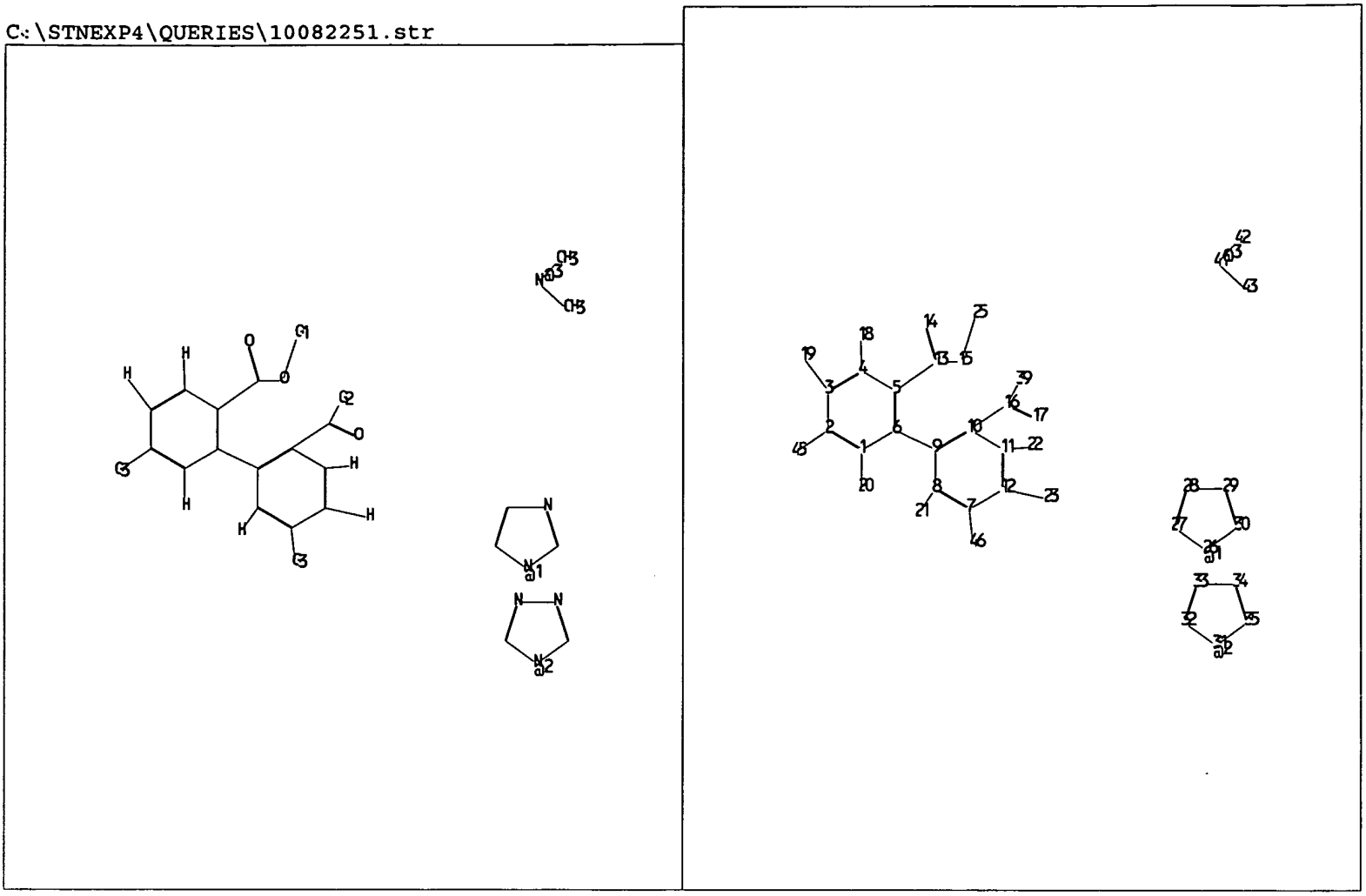

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13 14 15 16 17 18 19 20 21 22 23 25 39 41 42 43 45 46
ring nodes :
1 2 3 4 5 6 7 8 9 10 11 12 26 27 28 29 30 31 32 33 34 35
chain bonds :
1-20 2-45 3-19 4-18 5-13 6-9 7-46 8-21 10-16 11-22 12-23 13-14 13-15 15-25
16-17 16-39 41-42 41-43
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12 26-27 26-30 27-28
28-29 29-30 31-32 31-35 32-33 33-34 34-35
exact/norm bonds :
2-45 7-46 13-14 13-15 15-25 16-17 16-39 26-27 26-30 27-28 28-29 29-30 31-32
31-35 32-33 33-34 34-35
exact bonds :
1-20 3-19 4-18 5-13 6-9 8-21 10-16 11-22 12-23 41-42 41-43
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12

G1:H,CH3,Et,i-Pr,n-Bu,i-Bu,t-Bu

G2:OH,CN,[*1],[*2]

G3:H,CH3,MeO,CN,NH2,NO2,Cl,Br,[*3]

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom
12:Atom 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS 19:CLASS 20:CLASS
21:CLASS 22:CLASS 23:CLASS 25:CLASS 26:Atom 27:Atom 28:Atom 29:Atom 30:Atom
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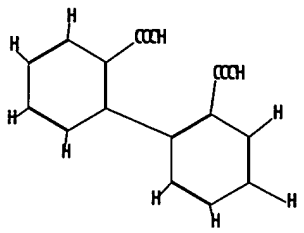

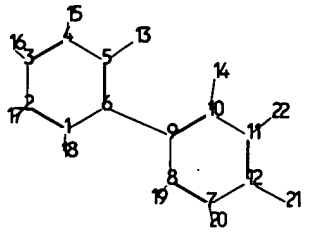

chain nodes :
13 14 15 16 17 18 19 20 21 22
ring nodes :
1 2 3 4 5 6 7 8 9 10 11 12
chain bonds :
1-18 2-17 3-16 4-15 5-13 6-9 7-20 8-19 10-14 11-22 12-21
ring bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12
exact bonds :
1-18 2-17 3-16 4-15 5-13 6-9 7-20 8-19 10-14 11-22 12-21
normalized bonds :
1-2 1-6 2-3 3-4 4-5 5-6 7-8 7-12 8-9 9-10 10-11 11-12

Match level :
1:Atom 2:Atom 3:Atom 4:Atom 5:Atom 6:Atom 7:Atom 8:Atom 9:Atom 10:Atom 11:Atom
12:Atom 13:CLASS 14:CLASS 15:CLASS 16:CLASS 17:CLASS 18:CLASS 19:CLASS 20:CLASS
21:CLASS 22:CLASS

10082251

=> d bib abs hitstr

L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2003:17318 CAPLUS
DN 138:72974
TI Preparation of **achiral** biaryl-type compounds, their use as chromophores for circular dichroism (CD), and determination of absolute configuration of chiral compounds
IN Ota, Tomihisa; Hosoi, Shinzo
PA Kanazawa University, Japan
SO Jpn. Kokai Tokkyo Koho, 18 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2003002871	A2	20030108	JP 2001-187770	20010621
	US 2003088104	A1	20030508	US 2002-82251	20020226
PRAI	JP 2001-187770	A	20010621		

OS MARPAT 138:72974
GI

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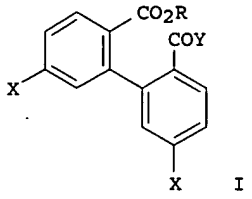
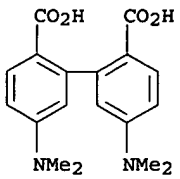


AB Detn. of abs. configuration of chiral alcs., thiols, or amines involves introduction of **achiral** biaryl compds. I (R = H, Me, Et, iso-Pr, n-Bu, iso-Bu, tert-butyl; X = H, Me, Me2N, MeO, NO2, NH2, CN, Cl, Br; Y = OH, CN, imidazol-1-yl, 1,3,4-triazol-1-yl; when R = H, Y = OH, then X = Me2N, CN; when R = Me, Y = OH, then X = Me, Me2N, NO2, NH2, CN; when R = Et, Y = OH, then X = Me, Me2N, MeO, NO2; X = H, Y = OH, then R = tert-butyl) or their analogs as CD chromophores to the chiral compds. and, is based on the relative bulk of the substituents in the .alpha. C, the priority in the CIP method, and the exciton chirality. Thus, l- or d-menthol was esterified with 3-cyanocarbonyl-3'-methoxycarbonyl-2,2'-binaphthalene in the presence of DMAP to give (R)- or (S)-ester, resp. Their exciton chirality was - and +, resp.

IT **482359-55-7 482359-57-9 482359-58-0**
482359-59-1 482359-60-4 482359-61-5
482359-62-6 482359-63-7 482359-64-8
482359-65-9 482359-66-0 482359-67-1
482359-68-2 482359-69-3
RL: RCT (Reactant); RACT (Reactant or reagent)
(prepn. of **achiral** biaryl-type compds. as CD chromophores for detn. of abs. configuration of chiral compds.)

RN 482359-55-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-bis(dimethylamino)- (9CI) (CA INDEX NAME)



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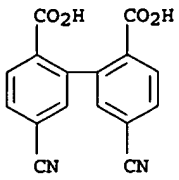

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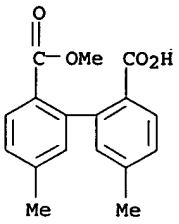

RN 482359-59-1 CAPLUS
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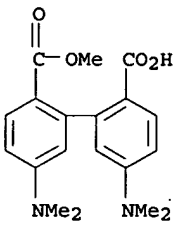

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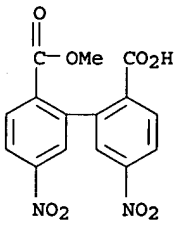

RN 482359-61-5 CAPLUS
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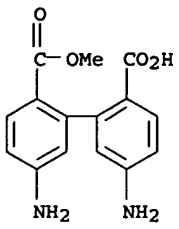

RN 482359-62-6 CAPLUS
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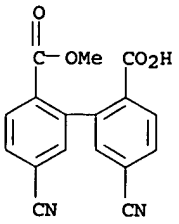

RN 482359-63-7 CAPLUS
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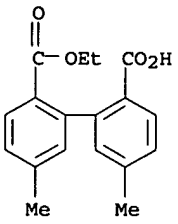

RN 482359-64-8 CAPLUS
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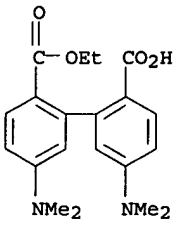

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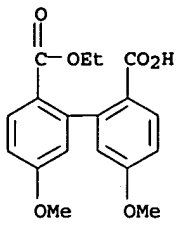

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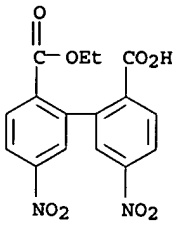

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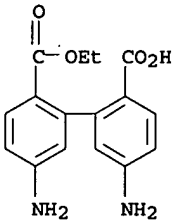

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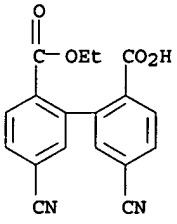
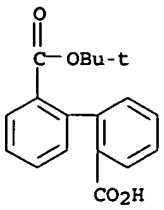


RN 482359-69-3 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, mono(1,1-dimethylethyl) ester (9CI) (CA INDEX NAME)

10082251



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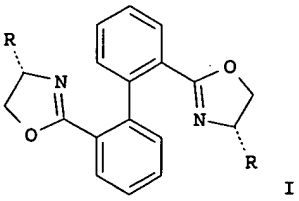
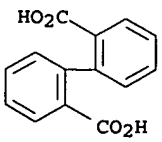
L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2000:301530 CAPLUS
DN 133:114068
TI Novel Chiral Bisoxazoline Ligands with a Biphenyl Backbone: Preparation, Complexation, and Application in Asymmetric Catalytic Reactions
AU Imai, Yoshitane; Zhang, Wanbin; Kida, Toshiyuki; Nakatsuji, Yohji; Ikeda, Isao
CS Department of Applied Chemistry Faculty of Engineering, Osaka University, Suita Osaka, 565-0871, Japan
SO Journal of Organic Chemistry (2000), 65(11), 3326-3333
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
GI



I

AB Novel C2-sym. chiral bisoxazoline ligands I (R = iPr, tBu, Ph, CH2Ph) were easily prepd. from enantiomerically pure 2-amino alcs. and **achiral** 2,2'-biphenyldicarboxylic acid via the corresponding amide and mesylate as intermediates. Since these ligands bear only two ortho-substituents on the biphenyl backbone, the biphenyl axis is not fixed, and the two diastereomers of these ligands exist in equil. in soln. Interestingly, when I were coordinated with a metal ion, only one of the two possible diastereomer complexes, an (S,aS,S)-complex, can be formed depending on the combination of the ligand and the metal ion. Thus, Cu(I) afforded only the (S,aS,S)-complexes with all ligands I, while Zn(II), Pd(II), and Ag(I) afforded the (S,aS,S)-complexes as the sole product only with I (R = tBu) and a mixt. of the two diastereomer complexes with I (R = iPr, Ph, CH2Ph). The Cu(I)-catalyzed asym. cyclopropanation of styrene with diazoacetate proceeded successfully with I and good to excellent enantioselectivities were afforded.
IT **482-05-3**, 2,2'-Biphenyldicarboxylic acid
RL: RCT (Reactant); RACT (Reactant or reagent)
(reactant for prepn. of bis(oxazolyl)biphenyl derivs.)
RN 482-05-3 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid (9CI) (CA INDEX NAME)



RE.CNT 53 THERE ARE 53 CITED REFERENCES AVAILABLE FOR THIS RECORD

10082251

=> d 1-3 bib abs hitstr

L29 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1994:301323 CAPLUS
DN 120:301323
TI Ink-jet printing ink compositions
IN Matsuzaki, Makoto; Kanbayashi, Kenichi
PA Seiko Epson Corp, Japan
SO Jpn. Kokai Tokkyo Koho, 8 pp.
CODEN: JKXXAF
DT **Patent**
LA Japanese
FAN.CNT 1

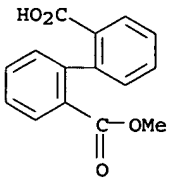
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 05339526	A2	19931221	JP 1992-145770	19920605

PRAI JP 1992-145770 19920605

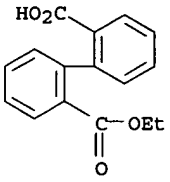
AB The compns. with water and abrasion resistance and good printability contain dyes and vehicles contg. biphenyl-2,2'-dicarboxylic acid esters with m.p. 50-150.degree.. Thus, biphenyl-2-2'-dicarboxylic acid monoethyl ester (m.p. 90-92.degree.) 80.0, a polyester resin 8.0, a polyester-polyol resin 8.5, C.I. Solvent Black 45 3.0, and antioxidant 0.5% was mixed to obtain an ink compn. showing good printability and water and abrasion resistance.

IT **6926-84-7**, Diphenic acid monomethyl ester **27428-70-2**
117354-45-7
RL: USES (Uses)
(vehicles contg. dyes and, for ink-jet printing inks, with water and friction resistance)

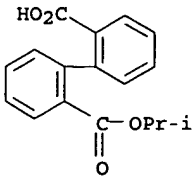
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



RN 27428-70-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester (9CI) (CA INDEX NAME)



RN 117354-45-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, mono(1-methylethyl) ester (9CI) (CA INDEX NAME)



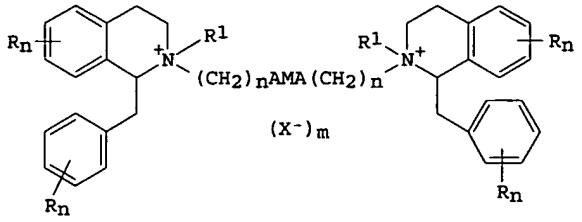
L29 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1994:134306 CAPLUS
DN 120:134306

10082251

TI Nitrogen bridge-containing tetrahydroisoquinoline muscle relaxants
IN Demko, Donald M.
PA Anaquest, Inc., USA
SO U.S., 15 pp. Cont.-in-part of U.S. Ser. No. 785,958, abandoned.
CODEN: USXXAM
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5240939	A	19930831	US 1992-977311	19921116
	EP 598171	A1	19940525	EP 1993-100350	19930112
	R: DE, ES, FR, GB, IT				
	JP 06157465	A2	19940603	JP 1993-9472	19930122
	CA 2088436	AA	19940517	CA 1993-2088436	19930129
PRAI	US 1991-785958		19911031		
	US 1992-977311		19921116		

OS MARPAT 120:134306
GI

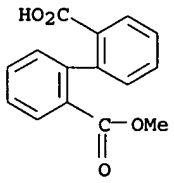


I

AB The title compds. I [A = CO2, O2C; M = (CH2)nZ(CH2)n; Z = (un)substituted amino, (un)substituted quaternary ammonium, (un)substituted acylamino, etc.; n = 1-6; R = C1-3 alkoxy, methylenedioxy; R1 = lower alkyl; X = pharmaceutically acceptable anion; m = 2, 3], useful as nondepolarizing neuromuscular blocking agents with short duration of activity and thus useful in short-term procedures (e.g., intubation of the trachea), are prepd. Thus, tetrahydropapaverine was condensed with 2-bromopropanol (sic), the intermediate condensed with acryloyl chloride, and the intermediate treated with isopropylamine, producing isopropyl-di-2-[3-(N-tetrahydropapaverinyl)propionyl]ethyl amine, which was quaternized with MeBr, producing N,N'-dimethyl-N,N'-3,11-dioxa-4,10-dioxo-7-isopropyl-7-methyl-7-azoniatridecylene-1,13-bis-tetrahydropapaverinium tribromide (II), m.p. 142-144.degree., in 86% yield. II demonstrated 90% neuromuscular junction blocking activity at 1.00 mg/kg in mice and 1.858 mg/kg in rabbits, vs. 0.020 and 0.012, resp., for pancuronium.

IT **6926-84-7P**, Diphenic acid monomethyl ester
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(prepn. and reaction of, in prepn. of nondepolarizing muscle relaxants)

RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



L29 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1988:595602 CAPLUS
DN 109:195602
TI Diphenic acid monoester soldering flux
IN Furuno, Megumi; Ito, Masao
PA Asahi Chemical Industry Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 4 pp.
CODEN: JKXXAF
DT Patent

10082251

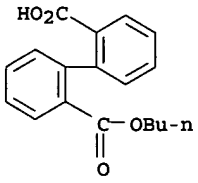
LA Japanese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 63132795	A2	19880604	JP 1986-278820	19861125
PRAI	JP 1986-278820		19861125		

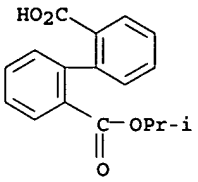
AB The diphenic acid monoester soldering flux is used on printed-circuit boards for easy cleaning with freon 113. The monoester is C3-18 alkyl monoalkyl ester. Thus, a soldering flux soln. contg. 30% diphenic acid monoiso-Pr ester and polymd. rosin in iso-PrOH was used in soldering an oxidized Cu plate using a soldering wire by heating at 260.degree.. The solder was spread at 96%, and elec. resistivity of iso-PrOH and tap water mixt. after extg. the soldered board cleaned with freon was 11.4 .times. 105 .OMEGA.-cm, compared with 89% and 6.5 .times. 105 .OMEGA.-cm for the polymd. rosin soln.

IT **27428-72-4 117354-45-7**
RL: USES (Uses)
(soldering fluxes contg., for printed-circuit boards for easy cleaning with freon)

RN 27428-72-4 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monobutyl ester (9CI) (CA INDEX NAME)



RN 117354-45-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, mono(1-methylethyl) ester (9CI) (CA INDEX NAME)



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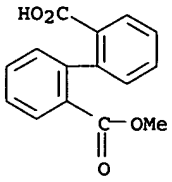
L31 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1969:501583 CAPLUS
DN 71:101583
TI Syntheses and properties of o-ketonic acids and their derivatives
AU Christiaens, L.; Renson, M.
CS Univ. Liege, Liege, Belg.
SO Bulletin des Societes Chimiques Belges (1969), 78(7-8), 359-93
CODEN: BSCBAG; ISSN: 0037-9646
DT Journal
LA French
GI For diagram(s), see printed CA Issue.
AB Mes = Mesityl in this abstr. Mixts. of I and II (R4 = OR) compds. are prepd.; it is proposed that the I are predominant in certain reactions and the II (R4 = OR) are the main product in other reactions. Also prepd. are III, IV, V, VI, VII, VIII, IX, and X compds. Thus, 8.8 g. 3,6-dimethylphthalic anhydride is treated with the Grignard prepd. from 12 g. 1-C10H7Br and 1.5 g. Mg to give 40 3,6-dimethyl-2-(1-naphthoyl)benzoic acid (XI), m. 186.degree.. Similarly prepd. is I (R = R2 = H, R1 = R3 = Ph) (XII), m. 172.degree.; XII is also prepd. from 3-phenylphthalic anhydride and Ph2Cd. XII gives 3,7-diphenyl-3-methoxyphthalide (m.150.degree.) and Me 6-phenyl-2-benzoylbenzoate (m. 93.degree.). Also prepd., according to the above, related, and known methods, are the following I (R = H, R3 = Ph) (R1, R2, and m.p. given): Mes, H, 225.degree.; Ph, Me, 210.degree.; Mes, Ph, 198.degree.; fluorenone-1-carboxylic acid (m. 197.degree.), III (R = Me, R1 = OH) (m. 205-6.degree.), the following I (R = Me) (R1, R2, R3, and m.p. given): 2-C10H7, H, H, 85.degree.; 1-C10H7,h, Me, 103-4.degree.; Mes, H, Ph, 105.degree.; Ph, Me, Ph 90.degree.; Mes,Me, Ph, 102.degree.; the following II (R4, R1, R2, R3 and m.p. given): OMe, Mes H, Ph, 160.degree.; OMe, Ph, Me, Ph, 191.degree.; OMe, 2-C10H7, H,H, 103.degree.; OMe, 1-C10H7, H, Me, 153.degree.; OAc, Ph, Me, H, 181.degree.; OAc, Ph, H, Me, 130.degree.; OAc, Ph, Me, Me, 175.degree.; OAc, Mes, Me, Me, 154.degree.; OAc, Ph, H, Ph, 196.degree.; OAc, Ph, Me, Ph, 172.degree.; OAc, Mes, Me, Ph, 185.degree.; 1-C10H7, Ph, H, H, 230.degree.; Ph, NHPh, H, Me, 206.degree.; Ph, Ph, Me, Me, 218.degree.; Ph, Ph, H, Ph, 195.degree.; Ph, NHPh, H, Ph, 215.degree.; Ph, Ph, Me, Ph, 255.degree.; 9-fluorenol-1-carboxylic acid (m. 194-5.degree.), the following IV (X, Y, R, and m.p. given): OAc, OH, H, 208.degree.; Cl, Cl, H, 160.degree.; OH, OH, Me, 195-6.degree.; OAc, OH, Me, 206.degree.; the following III (R, R1, and m.p. given): H, Ph, 120.degree.; H, Mes, 175.degree.; Me, Cl, 129.degree.; Me, OMe, 81.degree.; Me, Ph, 185.degree.; 3-mesito yl-2-naphthoic acid (m. 222.degree.), 1,2-BzC10H6CO2H (m. 222-3.degree.), 2,5-Me2 C6H3(CH2)3CO2H (m. 48.degree., Et ester b15 165.degree.), 5,8-dimethyl-3,4-dihydro-1,2-naphthalene-dicarboxylic anhydride (m. 187.degree.), 5,8,1,2-Me2C10H4(CO2H)2anhydride (m. 223.degree.), V (R = CO2H, R1 = Bz, R2 = H, R3 = R4= Me) (m. 212.degree.), V (R = Bz, R1 = CO2H, R2 = H, R3= R4 = Me) (m. 237.degree.), the following V (R, R1, R2, R3, R4, and m.p. given): H, Ac, CO2Me, H, H, 29.degree.; H, mesitoyl, CO2Me, H, H, 120.degree.; Bz, CO2Me, H, Me, Me, 145.degree.; CO2Me, Bz, H, Me, Me, 135.degree.; 1-methoxy-1-phenyl-3(1H)-oxonaphtho-[2,3-c]furan[sic] (m. 124-5.degree.), 1-acetoxy-1-phenyl-3(1H)-oxonaphtho[1,2-c]furan (m. 170.degree.), the following VI (R, R1, and m.p. given): (OAc, Me), O, 151.degree.; O, (Me, Me), 127.degree.; O, (Ph, Ph), 217.degree.; the following VII (R1 = O) (R and m.p. given): (Ph, H), 148.degree.; (Ph, Ph), 238.degree.; (H, H), 117.degree.; the following V (R, R1, R2, R3, R4, and m.p. given): H, CONH2, mesitoyl, H, H, 236.degree.; H, CONHPh, mesitoyl, H, H, 228.degree.; CO2H, H, H, H, mesitoyl, 255.degree.; CO2H, Me, H, H, COCH2Ph, 56.degree.; CO2H, Me, H, H, Bz, 199.degree.; CO2H, H, H, H, Ac, 93.degree.; CO2H, H, H, H, Bz, 147.degree.; CO2H, H, H, H, mesitoyl, 162.degree.; CO2H, Me, H, H, Bz, 127.degree.; 3-phenyl-3-propyl-1-oxo-1H,3H-naphtho[1,8=cd]-pyran (m. 141.degree.), the following VIII (R = Ph) (R1 and m.p. given): Ph, 203.degree.; SPh, 177.degree.; NH2, 205.degree.; NHPh, 212.degree.; 2'-methoxycarbonylbiphenyl-2-carboxylic acid (m.112.degree.), the following IX (R, R1, and m.p. given): CO2Me, COCl,-; CO2Me, C(O)SPh, 97.degree.; CO2Me, Ac, 78.degree.; CO2H, Ac, 122.degree.; CO2H, Bz, 83.degree.; CO2H, mesitoyl, 108.degree.; Ac, Ac, 83.degree.; Ac, Bz, 106.degree.; Bz, C(O)SPh, 119.degree.; Bz, CONHPh, 122.degree.; Bz, CONH2, 180.degree.; Bz, Bz, 166.degree.; mesitoyl, C(O)SPh, 168.degree.; mesitoyl, CONHPh, 194.degree.; 5,5-dimethyl-7-oxo-5,7-dihydrodibenz[c,e]oxepin (m. 125.degree.), the following X (R, R1, and m.p. given): Me, Ph, 152.degree.; Ph, Ph, 185.degree.; Ph, H, 129.degree.; 4-benzoylfluorenone (m. 93.degree.), and 8-methyl-2-phenyl-1-acenaphthenone (m. 121.degree.).
IT **6926-84-7P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

10082251

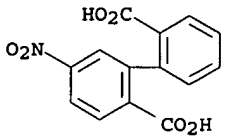
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



10082251

=> d 1-5, 10-15, 20-25, 30-32 bib abs hitstr

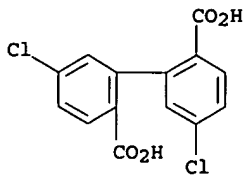
L33 ANSWER 1 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2000:669897 CAPLUS
DN 133:344984
TI A High-Affinity Fluorenone-Based .beta.2-Adrenergic Receptor Antagonist with a Photoactivatable Pharmacophore
AU Wu, Zhongren; Ruoho, Arnold E.
CS Department of Pharmacology, University of Wisconsin-Madison Medical School, Madison, WI, 53706-1532, USA
SO Biochemistry (2000), 39(42), 13044-13052
CODEN: BICHAW; ISSN: 0006-2960
PB American Chemical Society
DT Journal
LA English
AB To develop mols. capable of directly probing the catechol binding region of the .beta.2-adrenergic receptor (.beta.2AR), novel benzophenone- and fluorenone-based .beta.2AR antagonists were prepd. as potential photoaffinity probes. While the benzophenone-contg. ligands bound with relatively modest affinity, one of the fluorenone-based compds., 4-(2-hydroxy-3-isopropylaminopropoxy)-7-amino-6-iodofluorenone (iodoaminoflisopolol, IAmF), showed very high affinity for the .beta.2AR, inhibiting [125I]ICYP binding with an apparent Ki of approx. 1 .times. 10-9 M. In comparison to the benzophenone ligands, the fluorenone ligands have one addnl. carbon-carbon bond that creates a planar unsatd. ring system and leads to a large increase in receptor binding affinity. Unlike previous .beta.2AR photoaffinity ligands, an attractive and unique feature of the fluorenone deriv. IAmF is that the large planar unsatd. ring (believed to correspond to the catechol end of other .beta.2AR ligands) serves as both the binding pharmacophore and the photoreaction center for this mol. With this potential for directly probing the catechol binding region of the .beta.2AR, the authors synthesized and tested IAmF in carrier-free radioiodinated form ([125I]IAmF). When photoredn. was conducted at 350 nm for 20 min, [125I]IAmF was able to produce crosslinked products in both triethylamine and methanol, with a reactivity pattern similar to that found in benzophenone photochem. As a final test of suitability as a photoaffinity label, specific labeling of the .beta.2AR in membranes (protectable by 10 .mu.M alprenolol) was demonstrated. [125I]IAmF represents a new class of .beta.2AR photoaffinity labels that can directly probe the catechol-analogous antagonist pharmacophore binding site in the .beta.2AR ligand binding pocket.
IT **107943-42-0P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(high-affinity fluorenone-based .beta.2-adrenergic receptor antagonist with photoactivatable pharmacophore)
RN 107943-42-0 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5-nitro- (9CI) (CA INDEX NAME)



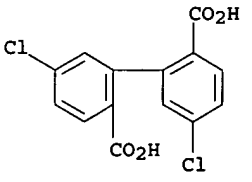
RE.CNT 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L33 ANSWER 2 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1997:481656 CAPLUS
DN 127:191916
TI A convenient route to 3,6-diaminofluoren-9-ones
AU Guinot, Stephane G. R.; Hepworth, John D.; Wainwright, Mark
CS Department Chemistry, University Central Lancashire, Preston, PR1 2HE, UK
SO Journal of Chemical Research, Synopses (1997), (6), 183
CODEN: JRPSDC; ISSN: 0308-2342
PB Royal Society of Chemistry
DT Journal
LA English
AB The synthesis of fluoren-9-ones having a 3,6-bis(tertiary amino) functionality is described, in which the amino groups are introduced using either cyclic secondary amines or their N-formylated derivs. to effect nucleophilic displacement of the halogen from 3,6-dichlorofluoren-9-one, which is derived from 4-chloroanthranilic acid.
IT **20872-11-1P**

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate; convenient route to 3,6-diaminofluoren-9-ones)
RN 20872-11-1 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dichloro- (9CI) (CA INDEX NAME)



L33 ANSWER 3 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1995:476541 CAPLUS
DN 124:55490
TI Synthesis of some N-substituted phenyl anthranilic acid derivatives and their immunostimulation effects
AU Wang, Shuqing; Ji, Zhizhong
CS Guangdong Coll. Petrochem. Technology, Maoming, 525000, Peop. Rep. China
SO Zhongguo Yaowu Huaxue Zazhi (1994), 4(4), 235-9, 244
CODEN: ZYHZEF; ISSN: 1005-0108
PB Zhongguo Yaowu Huaxue Zazhi Bianjibu
DT Journal
LA Chinese
AB Some N-substituted Ph anthranilic acid derivs. 2,5-(HO2C)ClC6H3NHR [R = 2,6-C6H3 (I), 3,4-ClFC6H3, 4-EtOC6H4 (II)] were prepd. and their immunostimulation effects were obsd. Lobenzarit was selected as the lead compd. and I (1 .mu.mol/L) and II (0.01 .mu.mol/L) obviously enhanced Con-A-induced proliferative responses of splenocytes from mice. II (1 .mu.mol/L) also increased ConA-induced interleukin-2 of lobenzarit. However, the i.p. LD50 of a single dose of II was 107.9 mg/kg. The margin of safety of II was narrower than that of lobenzarit. However, the i.p. LD50 of a single dose of II was 107.9 mg/kg. The margin of safety of II was narrower than that of lobenzarit.
IT **20872-11-1P**
RL: BYP (Byproduct); PREP (Preparation)
(synthesis of phenylanthranilic acid derivs. and their immunostimulation effects)
RN 20872-11-1 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dichloro- (9CI) (CA INDEX NAME)



L33 ANSWER 4 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1994:271845 CAPLUS
DN 120:271845
TI The synthesis of water-soluble, rigid-rod poly(p-phenylene) derivatives
AU Wallow, Thomas; Novak, Bruce M.
CS Dep. Chem., Univ. California, Berkeley, CA, 94720, USA
SO Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (1992), 33(1), 908-9
CODEN: ACPPAY; ISSN: 0032-3934
DT Journal
LA English
AB Poly(p-quaterphenylene-2,2'-dicarboxylic acid) was prepd. in aqua from water-sol. species of 4,4'-dibromobiphenyl-2,2'-dicarboxylic acid (I) and 4,4'-biphenylenebisboronic acid (II) in the presence of the water-sol. catalyst Pd[PPh2(m-C6H3SO3Na)]3 (III). Because this catalyst pptd. from soln. near the end of the reaction, 2 addnl. water-sol. catalysts possessing more basic phosphine ligands, i.e., Pd(PPh2CO2Na)3 and

Pd[P(p-C6H4OH)3]3, were prepd. and found to be active in the AA-BB polymn. of I and II. The degree of carboxylate substitution could be increased to 66%/phenyl ring by replacing II with 1,4-benzenediboronic acid. Crankshaft polymers were prepd. by polymg. II with 5,5'-dibromobiphenyl-2,2'-dicarboxylic acid. Evidence for a side reaction which scrambles the aryl groups during the coupling reaction was detected in the cross-coupling reaction of 3-bromobenzoic acid with 4-methylphenylboronic acid in the presence of III.

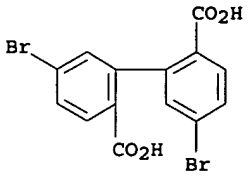
IT **154217-23-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of water-sol., catalysts for, palladium complexes as)

RN 154217-23-9 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dibromo-, polymer with [1,1'-biphenyl]-4,4'-diylbis[boronic acid] (9CI) (CA INDEX NAME)

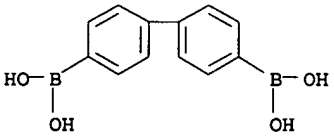
CM 1

CRN 13974-99-7
CMF C14 H8 Br2 O4



CM 2

CRN 4151-80-8
CMF C12 H12 B2 O4



L33 ANSWER 5 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1992:417744 CAPLUS

DN 117:17744

TI Structure and molecular chirality of the acetonitrile adduct of the 2:1 salt of quinidine with biphenyl-5,5'-dinitro-2,2'-dicarboxylic acid (5,5'-dinitrodiphenic acid)

AU Kubicki, Maciej; Borowiak, Teresa; Gawron, Marian

CS Fac. Chem., Adam Mickiewicz Univ., Poznan, 60-780, Pol.

SO Journal of Crystallographic and Spectroscopic Research (1992), 22(2), 205-11
CODEN: JCREDB; ISSN: 0277-8068

DT Journal

LA English

AB The mol. of the 2:1 salt consists of 2 quinidine cations and the 5,5'-dinitrodiphenic anion. Both of the quinidine cations are protonated at the N atoms of the quinuclidine fragments. Due to the interlocking H bonds between quinidine and the dinitrodiphenic ions, a rigid structure of the salt mol. has been formed. The alkaloid mol. conformation around the C(8)-C(9) bond is "open". The conformational parameters of 5,5'-dinitrodiphenic anion are considerably changed in comparison with the conformation of diphenic acid in the solid state. The abs. configuration of biphenyl-5,5'-dinitro-2,2'-dicarboxylic anion (R) is defined by the neg. torsion angles around the line which connects the centers of both Ph rings, and is the reverse of that obsd. in the diphenic acid-quinine salt. The present data confirm the observation that the chirality of the salt is controlled by the chirality of the Cinchona alkaloid mol. The title compd. is orthorhombic, space group P21212, with a 12.259(1), b 12.648(1), and c 17.380(2) .ANG.; Z = 2; final R = 0.061 (Rw = 0.081). At. coordinates are given.

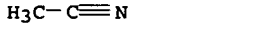
IT **141893-71-2**, Quinidine compd. with 5,5'-dinitrodiphenic acid and acetonitrile (2:1:2)

10082251

RL: PRP (Properties)
(crystal structure and mol. chirality of)
RN 141893-71-2 CAPLUS
CN Cinchonan-9-ol, 6'-methoxy-, (9S)-, 5,5'-dinitro[1,1'-biphenyl]-2,2'-dicarboxylate, compd. with acetonitrile (2:1:2) (9CI) (CA INDEX NAME)

CM 1

CRN 75-05-8
CMF C2 H3 N

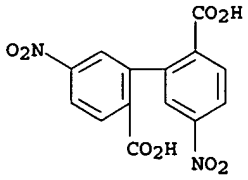


CM 2

CRN 125707-61-1
CMF C20 H24 N2 O2 . 1/2 C14 H8 N2 O8

CM 3

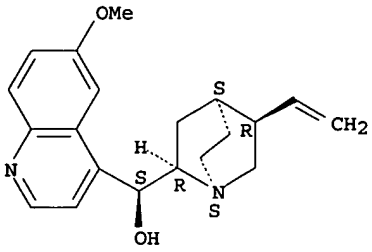
CRN 92159-34-7
CMF C14 H8 N2 O8



CM 4

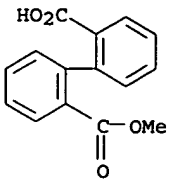
CRN 56-54-2
CMF C20 H24 N2 O2

Absolute stereochemistry. Rotation (+).

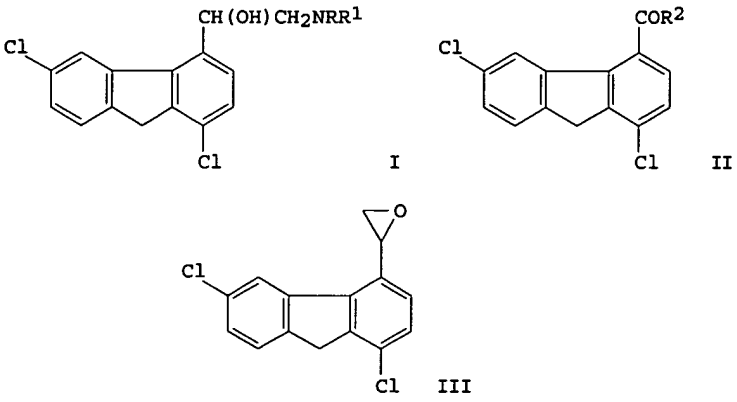


L33 ANSWER 10 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1985:5589 CAPLUS
DN 102:5589
TI Dissociation of benzenecarboxylic acid derivatives in mixture media
AU Benko, Jan; Dlha, Helena; Foltin, Miloslav
CS Dep. Phys. Chem., Univ. Komensky, Bratislava, 842 15, Czech.
SO Acta Facultatis Rerum Naturalium Universitatis Comenianae, Chimia (1984), 32, 115-26
CODEN: AFRCAQ; ISSN: 0524-2312
DT Journal
LA English
AB The solvent effect on the dissocn. consts. of RC6H4CO2H (R = H, 2-, 3-, or 4-OH or -MeO2C, 3- or 4-NO2, 4-Cl, 4-NH2) and mono-Me diphenate [detd. using an LFER for the mol fraction of org. solvent in aq. MeOH, aq. PrOH, aq. Me2CHOH, and aq. Me3COH] was related to the alternation of solvent structure. The acids were least dissocd. at mol fraction corresponding to the most disordered solvent structure.
IT **6926-84-7**
RL: PROC (Process)

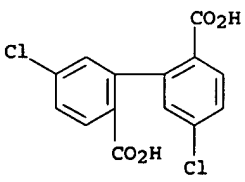
(dissocn. of, in aq. alc. binary mixts., solvent effects and)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



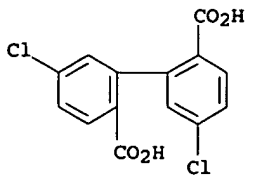
L33 ANSWER 11 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1982:199248 CAPLUS
DN 96:199248
TI Studies on antimalarials. II. Synthesis of .alpha.-alkylaminomethyl-1,6-dichloro-4-fluorenemethanols
AU Zhao, Dechang; Zhong, Jingxing; Geng, Rongliang; Li, Guofu; Ding, Deben; Deng, Rongxian
CS Inst. Microbiol. Epidemiol., Milit. Acad. Med. Sci., Beijing, Peop. Rep. China
SO Yaoxue Xuebao (1982), 17(1), 28-32
CODEN: YHHPAL; ISSN: 0513-4870
DT Journal
LA Chinese
GI



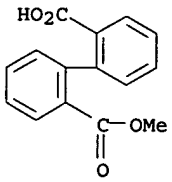
AB Fluorenemethanol derivs. (I; R, R1 = alkyl, NRR1 = pyrrolidino, morpholino), effective antimalarials at 25 mg/kg, were prepd. Thus, chlorination of 6.5 g acid II (R2 = OH) with SOCl2 followed by reaction with CH2N2 and 48% HBr gave 6.4 g bromoacetyl deriv. II (R2 = BrCH2), which (200 mg) was reduced with NaBH4 in MeOH at 10-45.degree. to give 120 mg oxirane deriv. III. Reaction of III with RR1NH followed by anhyd. HCl-Et2O gave I HCl.
IT **20872-11-1**
RL: RCT (Reactant); RACT (Reactant or reagent)
(intramol. cyclocondensation of)
RN 20872-11-1 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dichloro- (9CI) (CA INDEX NAME)



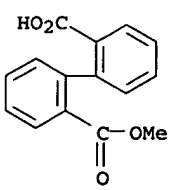
10082251



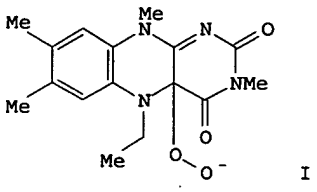
L33 ANSWER 12 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1981:496466 CAPLUS
DN 95:96466
TI Kinetics of the alkaline hydrolysis of semiesters of dicarboxylic acids in electrolyte solutions
AU Holba, Vladislav; Benko, Jan; Komadel, Peter
CS Fak. Komensky-Univ., Bratislava, 81650, Czech.
SO Zeitschrift fuer Physikalische Chemie (Leipzig) (1981), 262(3), 445-8
CODEN: ZPCLAH; ISSN: 0372-9680
DT Journal
LA German
AB Rate consts. were detd. for the hydrolysis of mono-Me phthalate, mono-Me 2,2'-biphenyldicarboxylate, and mono-Me terephthalate (I) in the presence of Me4NBr and several inorg. Na salts. Both the cation and the anion of the added salt affected the hydrolysis rate. In the case of I the effects resulted from the H2O structure-breaking or structure-forming properties of the salt.
IT **6926-84-7**
RL: RCT (Reactant); RACT (Reactant or reagent)
(sapon. of, salt effect on)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 13 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1980:549338 CAPLUS
DN 93:149338
TI Medium effect on alkaline hydrolysis of diphenic acid monomethyl ester
AU Benko, Jan; Holba, Vladislav
CS Dep. Phys. Chem., Comenius Univ., Bratislava, 816 50, Czech.
SO Collection of Czechoslovak Chemical Communications (1980), 45(5), 1485-94
CODEN: CCCCAK; ISSN: 0366-547X
DT Journal
LA English
AB The kinetic consts., activation energies, and entropies of the sapon. of 2-(2-HO2CC6H4)C6H4CO2Me in mixts. of H2O with ROH (R = Me, Et, Pr, Me2CH, Me3C), and Me2CO were detd. Nonaq. solvents decrease the reverse decompn. of the activated complex which is stabilized by intramol. H bonding.
IT **6926-84-7**
RL: RCT (Reactant); RACT (Reactant or reagent)
(sapon. of, solvent effects on kinetics of)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)

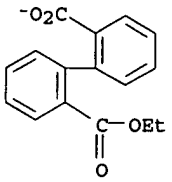


L33 ANSWER 14 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1980:549322 CAPLUS
DN 93:149322
TI Dioxygen transfer from 4a-hydroperoxyflavin anion. 2. Oxygen transfer to the 10 position of 9-hydroxyphenanthrene anions and to 3,5-di-tert-butylcatechol anion
AU Muto, Shigeaki; Bruice, Thomas C.
CS Dep. Chem., Univ. California, Santa Barbara, CA, 93106, USA
SO Journal of the American Chemical Society (1980), 102(13), 4472-80
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA English
GI



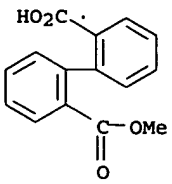
I

AB Reaction of peroxy anion I with the anions of 3,5-di-tert-butylcatechol (II) and 10-ethoxy- (III) and 10-methyl-9-phenanthrol (IV) was studied. All products were accounted for via O2 transfer from I to the phenolate anions with the prodn. of reduced flavin anion and a hydroperoxycyclohexadienone.
IT **74976-73-1P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 74976-73-1 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester, ion(1-) (9CI) (CA INDEX NAME)

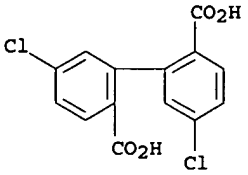


L33 ANSWER 15 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1980:180292 CAPLUS
DN 92:180292
TI Kinetics of alkaline hydrolysis of diphenic and terephthalic acid monomethyl esters
AU Holba, Vladislav; Benko, Jan; Kozankova, Jana
CS Fac. Nat. Sci., Comenius Univ., Bratislava, 816 50, Czech.
SO Collection of Czechoslovak Chemical Communications (1980), 45(1), 255-62
CODEN: CCCCAK; ISSN: 0366-547X
DT Journal
LA English
AB The dependencies of the hydrolysis rates of the title esters on temp. and concns. of 14 electrolytes were detd. From the rate consts. extrapolated to zero ionic strength, activation energy and entropy, frequency factor, and crit. interionic distance in the activated complex were calcd.
IT **6926-84-7**
RL: PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process); RACT (Reactant or reagent)
(hydrolysis of, kinetics of)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)

10082251

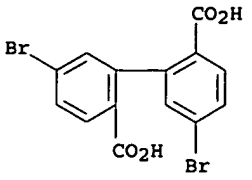


L33 ANSWER 20 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1969:3471 CAPLUS
DN 70:3471
TI 5,5'-Disubstituted diphenic acid derivatives
AU Weis, C. D.
CS Forschungslab., J. R. Geigy A.-G., Basel, Switz.
SO Helvetica Chimica Acta (1968), 51(7), 1582-7
CODEN: HCACAV; ISSN: 0018-019X
DT Journal
LA German
GI For diagram(s), see printed CA Issue.
AB 5,5'-Dichloro-2,2'-bi-phenyldicarboxylic acid (I) is readily accessible by oxidn. of 3,6-dichloro-9,10-phenanthrenequinone, in turn prepd. from DDT. Various substitutions and transformations of I and its derivs. are reported.
IT **20872-11-1P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 20872-11-1 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dichloro- (9CI) (CA INDEX NAME)



L33 ANSWER 21 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1967:115495 CAPLUS
DN 66:115495
TI Conjugation in macrocyclic bonding systems. VIII. Alkyl-substituted hexa- and octa-m-phenylenes
AU Braeunling, Hermann; Binnig, Fritz; Staab, Heinz A.
CS Univ. Heidelberg, Heidelberg, Fed. Rep. Ger.
SO Chemische Berichte (1967), 100(3), 880-8
CODEN: CHBEAM; ISSN: 0009-2940
DT Journal
LA German
GI For diagram(s), see printed CA Issue.
AB cf. CA 66, 65196a. Alkyl derivs. of hexa-m-phenylene and octa-m-phenylene were prepd. Thus, the di-Grignard deriv. of 3,3'-dibromo-5,5'-dimethylbiphenyl treated with excess CuCl2 in tetrahydrofuran gave 5,51,52,53,54,55-hexamethylhexa-m-phenylene. Similarly was prepd. 9,10,91,101,92,102-hexahydro-3,61:31,62:32,6-triphenanthrylene (I) starting from 3,6-dibromo-9,10-dihydrophenanthrene. Treatment of the di-Grignard deriv. of 5,51-dibromo-2,21-dimethylbiphenyl with CuCl2 led to 4,61,42,63,44,65,46,67-octamethylocta-m-phenylene instead of the expected 4,61,42,63,44,65-hexamethylhexa-m-phenylene. The uv. mass, and proton resonance spectra are given for the compds.
IT **13974-99-7P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 13974-99-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dibromo- (9CI) (CA INDEX NAME)

10082251



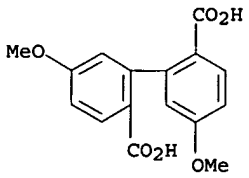
L33 ANSWER 22 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1964:476738 CAPLUS
DN 61:76738
OREF 61:13357c-h,13358a-f
TI Galanthamine chemistry. V. Formation of hydroxyapogalanthamine from galanthaminone and the synthesis of its trimethyl ether
AU Koizumi, Junji; Kobayashi, Shigeru; Uyeo, Shojiro
CS Nippon Shinyaku Co., Kyoto, Japan
SO Chemical & Pharmaceutical Bulletin (1964), 12(6), 696-705
CODEN: CPBTAL; ISSN: 0009-2363
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB cf. CA 50, 16803f; 51, 9649e. The structure of galanthamine (I) was verified. The structure of hydroxyapogalanthamine (II), the product of a dienone-phenol rearrangement, was elucidated by degradation reactions and confirmed by synthesis of its trimethyl ether. Treatment of 100 mg. galanthaminone (III) with 46% HBr (5 hrs. at 100.degree., sealed tube) gave 70 mg. III O-demethyl deriv. III (600 mg.) was refluxed 40 min. with 15 ml. HI (b. 127.degree.) and 200 mg. red P to give 250 mg. II.HI, m. 263-5.degree. (abs. alc.). Methylation of 300 mg. II.HI with CH_2N_2 gave 200 mg. II trimethyl ether (IV); perchlorate m. 163-5.degree. (alc.); methiodide m. 232-5.degree. (MeOH-ether). IV (150 mg.) was stirred in water 1 hr. with Ag_2O, filtered, the filtrate evapd. to dryness, and the residue heated 3 hrs. at 100.degree., and extd. with $CHCl_3$ to give 90 mg. viscous oil. This (in C_6H_6) was oxidized with $KMnO_4$ (3 hrs. at 80.degree. and 2 hrs. at 95.degree.) to give 40 mg. 5,5',6'-trimethoxy-2,2'-biphenyldicarboxylic acid (V). The Ullmann condensation of 3 g. Me 2-bromoveratrate (VI) with 2.5 g. Me 2-iodoanisate gave the di-Me ester of V 6-Me deriv. (VII), m. 138-40.degree.. The ether-sol. fraction gave liquids (VIII and IX), b0.02 150-60.degree. and b0.02 170-80.degree., resp. Sapon. of VIII and IX gave, resp., 0.4 g. 5,5'-dimethoxy-2,2'-biphenyldicarboxylic acid, m. 176-8.degree. (AcOEt), and V. Ullmann condensation of 4 g. VI with 7.5 g. 2-iodo-4-methoxytoluene gave VII and 1.5 g. (crude) X, m. 100-101.5.degree. (ether). Sapon. of 0.1 g. X gave 70 mg. corresponding acid, m. 139-41.degree. (ether). Treating 0.3 g. X with N-bromosuccinimide and Bz_2O_2 and heating the product with KCN in alc. gave 60 mg. XI, m. 103-5.degree.. XI was also prepd. by Ullmann condensation of 9 g. VI and 12 g. 2-iodo-4-methoxybenzaldehyde (XII) which gave 0.7 g. VII, 0.7 g. 5,5' dimethoxy-2,2'-biphenyldicarboxaldehyde, m. 100-2.degree. (MeOH) (also prepd. by heating XII at 200.degree. with Cu bronze), and 3.1 g. XI. Hydrolysis of XI with $Ba(OH)_2$ in alc. gave the acid, m. 149-51.degree.. Redn. of XI with Pd-C gave X. Oxidn. of 2.7 g. XI in acetone with $KMnO_4$ at 55-60.degree. gave 2.1 g. XIII, m. 163-5.degree.. Hydrolysis of XIII gave V. Treatment of XIII with $(COCl)_2$ gave the acid chloride which was treated with CH_2N_2 to give the diazo ketone. This was treated with BzOAg and Et_3N in MeOH to give 53% XIV (purified by chromatography on alumina), m. 88-9.degree. (MeOH-petr. ether). Hydrolysis of XIV gave the dicarboxylic acid (XV), m. 235-7.degree. (alc.). The Ullmann condensation of 2 g. VI and 2.7 g. Me 2-iodo-4-methoxyphenylacetate (XVI) gave 0.3 g. VII and 0.8 g. of an oil, b0.18 203-10.degree.. This oil was triturated with ether, VII filtered off, the filtrate concd., and the residue hydrolyzed to give 30 mg. XV. XV and CH_2N_2 gave XIV. 2-Iodo-4-methoxybenzoic acid (2.9 g.) and $SOCl_2$ gave the acid chloride which was treated with CH_2N_2 to give 2 g. 2-iodo-4-methoxy-2'-diazoacetophenone (XVII), m. 67-8.5.degree. (ether). XVII (0.55 g.) was treated with BzOAg and Et_3N, and the product hydrolyzed with KOH-alc. to give 0.4 g. 2-iodo-4-methoxyphenylacetic acid, m. 112-14.degree.. Esterification of 10 g. of this acid gave 7.45 g. XVI, b0.2 130-2.degree.. Redn. of XIV with $LiAlH_4$ in ether gave XVIII, m. 90-2.degree. (etherpetr. ether). XVIII (0.4 g.) and PBr_3 gave the dibromide which was heated in a sealed tube 4 hrs. at 130.degree. with 8 g. $MeNH_2$ and 15 ml. MeOH. The resultant base, 6-methyl-1,2,11-trimethoxy-5,6,7,8-tetrahydrodibenz[c,e]azocine (XIX), was converted into the styphnate (40 mg.), m. 178-81.degree., and perchlorate, m. 167-70.degree.. The styphnate salt was identical with O,O,O-trimethylhydroxyapogalanthamine styphnate. XI (0.55 g.), 1.5 g. $MeNO_2$, and 0.7 g. $AcONH_4$ in 18 ml. AcOH

was heated 9 hrs. at 100.degree. in a sealed tube. Solvent was removed, water added, the mixt. extd. with C6H6, and the ext. concd. to give 320 mg. XX, m. 124-6.degree. (ether). LiAlH4 redn. of 0.35 g. XX in ether gave 0.28 g. XXI. Treatment of 0.32 g. XXI with PBr3 gave 0.32 g. of the bromide which was refluxed 2 hrs. with 2 g. KOH and 35 ml. MeOH. The solvent was evapd. off and the residue extd. with 8% HCl. The HCl ext. was made alk. with Na2CO3 and extd. with CHCl3, the CHCl3 residue in C6H6 passed through a column of alumina, and the eluate converted to its styphnate to give 1,2,11-trimethoxy-5,6,7,8-tetrahydrodibenz [c,e] azocine styphnate (120 mg.) (XXII), m. 212-15.degree. (alc.). Methylation of 40 mg. XXII with HCO2H and HCHO gave 20 mg. XIX styphnate. NaOEt, III, and piperonal in alc. (room temp. overnight) gave III piperonylidene deriv., m. 252-4.degree. (acetone-MeOH). Oxolycoramine (XXIII) (lycoramine lactam) (200 mg.) was mixed with 200 mg. 30% Pd-C, the mixt. dried in a desiccator and heated at 300.degree. under N, then extd. with CHCl3. The CHCl3 residue was chromatographed in C6H6 over Al2O3. With reaction times of 5 min. (a), 20 min. (b), 30 min. (c), and 60 min. (d) the products were: (a) a trace of deoxyoxolycoramine (XXIV) and 95 mg. oxolycoraminone (XXV), m. 215-19.degree. (alc.); (b) 20 mg. XXIV, m. 148-50.degree. (alc.), and 50 mg. XXV; (c) 50 mg. XXIV; (d) 15 mg. XXIV and an unidentified nonbasic product, b0.02 120-30.degree.. XXIII (100 mg.) in 3 ml. AcOH satd. with HBr was heated 3 hrs. at 100.degree. in a sealed tube to give 100 mg. solid, m. 234-5.degree.. This was refluxed 1 hr. with 7 ml. 20% NaOH, 5 g. Zn dust, and 30 ml. alc., filtered, concd. to 10 ml., 10 ml. water added, CO2 bubbled in to pH 8.0, and the soln. extd. with CHCl3 to give demethyldeoxyoxolycoramine (XXVI), m. 265-6.5.degree. (alc.). Treatment of XXVI with CH2N2 gave XXIV.

IT **6787-56-0**, Diphenic acid, 5,5'-dimethoxy-
(prepn. of)

RN 6787-56-0 CAPLUS

CN Diphenic acid, 5,5'-dimethoxy- (6CI, 7CI, 8CI) (CA INDEX NAME)



L33 ANSWER 23 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1963:47323 CAPLUS

DN 58:47323

OREF 58:8095c-d

TI Effect of plasticizer structure on the glass-transition tem- perature of polymers. II. Plasticization of poly(methyl methacrylate) by esters of diphenic and naphthalic acids

AU Tager, A. A.; Suvorova, A. I.; Goldyrev, L. N.; Esafov, V. I.; Topina, L. P.

SO Vysokomolekulyarnye Soedineniya (1962), 4, 809-14
CODEN: VMSDA8; ISSN: 0042-9368

DT Journal

LA Unavailable

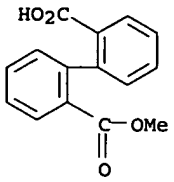
AB The effect of diesters of I and II and of monoesters of I on the Tg of poly(Me methacrylate) was investigated. The value of Tg gradually diminishes with increased size of the alkyl radical in mols. of diphenates and phthalates. In the case of naphthalates, Tg first decreases, but above 4 CH2 groups/mol., it increases. A sharp difference between the plasticizing abilities of diphenic and naphthalic esters was observed. For polystyrene and poly(Me methacrylate), the relation between the plasticizing effect of a compd. and its compatibility with the polymer and also the role of aromatic nuclei in the mols. of plasticizer were discussed. The molar concn. rule does not seem to be valid for the polymer-plasticizer systems investigated.

IT **6926-84-7**, Diphenic acid, methyl ester **27428-70-2**, Diphenic acid, ethyl ester **27428-72-4**, Diphenic acid, butyl ester
(plasticization of Me methacrylate polymers by, vitrification temp. and)

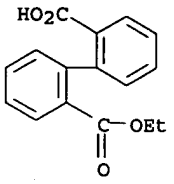
RN 6926-84-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)

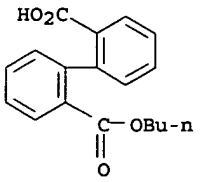
10082251



RN 27428-70-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester (9CI) (CA INDEX NAME)

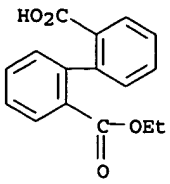


RN 27428-72-4 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monobutyl ester (9CI) (CA INDEX NAME)

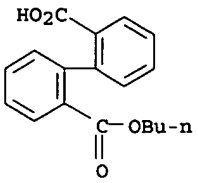


L33 ANSWER 24 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1963:47322 CAPLUS
DN 58:47322
OREF 58:8095a-c
TI Effect of plasticizer structure on the glass-transition tem- perature of polymers. I. Plasticization of polystyrene by esters of diphenic and naphthalic acids
AU Tager, A. A.; Suvorova, A. I.; Goldyrev, L. N.; Esafov, V. I.; Berestova, V. L.
SO Vysokomolekulyarnye Soedineniya (1962), 4, 803-8
CODEN: VMSDA8; ISSN: 0042-9368
DT Journal
LA Unavailable
AB The effect of the diesters of diphenic (I) and naphthalic (II) acids and the monoesters of diphonic acid on the glass-transition temp. (Tg) of polystyrene was investigated. A relation between the plasticizing capacity of the plasticizer and its compatibility with poly-styrene was found (the lower the crit. mixing temp., the lower the Tg). The value of Tg gradually decreased with increased size of alkyl radicals in the ester. In the case of diesters of I, Tg begins to increase from 10 CH2 groups. Monoesters of I are poor plasticizers for polystyrene; diesters of II lower the Tg much less than those of diphenic acid
IT **27428-70-2**, Diphenic acid, ethyl ester **27428-72-4**, Diphenic acid, butyl ester
(plasticization of Me methacrylate polymers by, vitrification temp. and)
RN 27428-70-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester (9CI) (CA INDEX NAME)

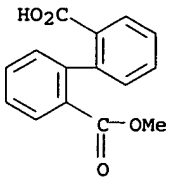
10082251



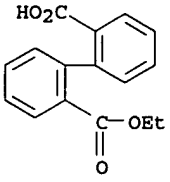
RN 27428-72-4 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monobutyl ester (9CI) (CA INDEX NAME)



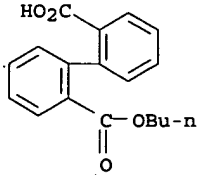
IT **6926-84-7**, Diphenic acid, methyl ester **27428-70-2**, Diphenic acid, ethyl ester **27428-72-4**, Diphenic acid, butyl ester
(plasticization of styrene polymers by, vitrification temp. and)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



RN 27428-70-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester (9CI) (CA INDEX NAME)



RN 27428-72-4 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monobutyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 25 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1961:27707 CAPLUS
DN 55:27707

10082251

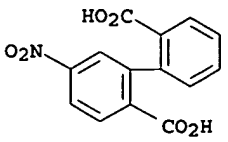
OREF 55:5414g-i,5415a-g
TI Orientation effects in the diphenyl (biphenyl) series. XV. Derivatives of 2,2'-bitolyl and of 2,2',4,4'-tetramethylbiphenyl
AU Everitt, Pauline M.; Loh, Shiu May; Turner, E. E.
CS Bedford Coll., London
SO Journal of the Chemical Society, Abstracts (1960) 4587-90
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA Unavailable
AB cf. CA 50, 2504d. Nitration of m-tolidine (I) in the presence of excess concd. H_2SO_4 occurred in position 5. 5-Nitro-2,2'-bitolyl (II) and 2,2',4,4'-tetramethyl-6-nitrobiphenyl (III) were prepd. and reduced to the corresponding amines. Redn. of m-$O_2NC_6H_4Me$ in alc. with Zn dust and NaOH and then rearrangement in acid gave 55% m-tolidine (IV), plates, m. 87-8.degree. (C_6H_6). IV diazotized at 0.degree. to -5.degree. in HCl and kept 15 hrs. with 50% hypophosphorus acid gave 52% 2,2'-bitolyl, b1-5 110-13.degree., m. 18.degree.. IV (106 g.) in 700 cc. H_2SO_4 stirred and treated at 0.degree. to -5.degree. with 50.5 g. KNO_2 during 2 hrs., the soln. poured onto ice, the sulfate filtered off, the solid ground with 30% NaOH, and the liberated base crystd. gave 364 g. 5-nitro-m-tolidine (V), m. 173-5.degree.. V was diazotized in HBr at 0.degree. to -5.degree. and the diazo soln. added slowly to a cold suspension of CuBr in HBr (the reaction was complete in 1 hr. at 100.degree.) and the product crystd. gave 4,4'-dibromo-5-nitro-2,2'-bitolyl (VI), m. 100-1.degree.(alc.). VI (0.4 g.) in 1 cc. piperidine warmed 5 min. on the steam bath gave 6.9 g. 4-bromo-5'-nitro-4'-piperidino-2,2'-bitolyl, m. 105-7.degree. (alc.). V (85.7 g.) diazotized in HCl and the diazo soln. treated with hypophosphorous acid, after several hrs. the product dissolved in Et_2O and washed, and the residue distd. in vacuo gave II, m. 65-6.degree.. A total of 340 g. V gave 133.5 g. II. Catalytic redn. of II in alc. and purification via the HCl salt gave 70% 5-amino-2,2'-bitolyl (VII), flakes, m. 59-60.degree. (dil. alc.). The benzoyl deriv. of II formed needles, m. 129-30.degree. (dil. alc.); p-nitrobenzoyl deriv., yellow plates, m. 160-1.degree.; formyl deriv. m. 124-6.degree.; acetyl deriv., needles, m. 131-3.degree. (ligroine). VII in C_6H_6 with aq. alkali treated gradually with Me_2SO_4 gave 61% 5-dimethylamino-2,2'-bitolyl (VIII), b7 146-8.degree.. VIII readily combined with MeI at room temp. to give the quaternary iodide, m. 177-8.degree.. Oxidn. of II with alk. $KMnO_4$ (6 hrs.) gave a 29% yield of 5-nitrodiphenic acid (IX), m. 266-7.degree. (dil. alc.). IX refluxed 1 hr. with Ac_2O gave the anhydride, m. 194-5.degree.. IX was decarboxylated by refluxing 1 hr. in quinoline over Cu powd.; the product poured into acid, extd. with Et_2O; evapd. and steam distd. gave 3-nitrobiphenyl, m. 63-4.degree.. Na_2S redn. of 6,6'-dinitro-2,2'-bitolyl gave a 66% yield of 6-amino-6'nitro-2,2'-bitolyl (X), m. 123-4.degree.. X (4.8 g.) in 5 cc. hot concd. HCl and 20 cc. H_2O diazotized at 0-5.degree. with 1.52 g. $NaNO_2$ (0.5 hr.), hypophosphorous acid added, the product kept overnight at 0.degree., extd. with Et_2O, washed, evapd., the residue steam distd. from alk. soln., and the product crystd. gave 2.3 g. 6-nitro-2,2'-bitolyl (XI), flakes, m. 42-3.degree.. Catalytic redn. of XI in alc. and purification via the HCl salt gave 6-amino-2,2'-bitolyl, m. 27.degree. (ligroine). 2-Iodo-1,5-dimethyl-3-nitrobenzene (50 g.) at 130-5.degree. was gradually treated with 50 g. Cu powder; after 1 hr., the mixt. heated 0.5 hr. at 155-60.degree. and the product extd. with PhCl gave 85% 2,2',4,4'-tetramethyl-6,6'-dinitrobiphenyl (XII), prisms, m. 136-7.degree. (alc. or C_6H_6). XII (60 g.) in 600 cc. refluxing alc. was treated during 15 min. with 57.6 g. $Na_2S.9H_2O$ and 15.4 g. S in 150 cc. H_2O, the mixt. refluxed 3 hrs., concd., and cooled, and the solid filtered off and extd. with refluxing dil. HCl. The HCl salt was readily hydrolyzed by H_2O to give 6-amino-2,2',4,4'-tetramethyl-6'-nitrobiphenyl (XIII), needles, m. 117-18.degree. (alc.). XIII was diazotized in dil. HCl and the soln. treated with hypophosphorous acid (addn. of Cu powder accelerated the reaction, which was complete in 1 hr. at 15-20.degree.); steam distn. gave 54% III, yellow rhombs, m. 107-8.degree. (alc.). III was reduced either catalytically or by $SnCl_2$ and HCl. Catalytic redn. was preferred, since work-up was more rapid and the yield nearly quant. In the catalytic redn. of 10 g. III, the residue (after evapn. of the alc.) treated with concd. HCl gave the solid 6-amino-2,2',4,4'-tetramethylbiphenyl (XIV) as the HCl salt. XIV was liberated by NH_3 and extd. with Et_2O to give 96% XIV, m. 50-1.degree.. XIV treated with C_5H_5N and p-nitrobenzoyl chloride gave 75% 2,2',4,4'-tetramethyl-6-(p-nitrobenzamido)biphenyl (XV), yellow prisms, m. 140-1.degree. (alc.). XV (8 g.) and 16 g. $POCl_3$ in 25 cc. $PhNO_2$ heated 12 hrs. at 175-80.degree., the product poured into alkali, the mixt. steam distd., and the product crystd. gave 78% 2,4,5,7-tetramethyl-9-(p-nitrophenyl)phenanthridine (XVI), flat needles, m. 159-60.degree., or rhombs, m. 177-8.degree.. XVI (7.3 g.) in 40 cc. AcOH treated at 70.degree. with 15 g. $SnCl_2.2H_2O$ in 18 cc. concd. HCl, the soln. refluxed 15 min., heated on the H_2O bath 45 min., and poured into excess 10% NaOH,

the solid collected and dissolved in dil. HCl, and the amine repptd. with alkali gave 77% 9-(p-aminophenyl)-2,4,5,7-tetramethylphenanthridine, yellow prisms, m. 195-6.degree. (C6H6-ligroine).

IT 107943-42-0, Diphenic acid, 5-nitro-
(prepn. of)

RN 107943-42-0 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5-nitro- (9CI) (CA INDEX NAME)



L33 ANSWER 30 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1955:39430 CAPLUS

DN 49:39430

OREF 49:7552d-i,7553a-d

TI Photochemical reactions. IV. The photosynthesis of cyclic sulfuric acid esters by the addition of SO2 to o-quinones

AU Schenck, Gunther O.; Schmidt-Thomee, Georg A.

CS Univ. Gottingen, Germany

SO Ann. (1953), 584, 199-220

DT Journal

LA Unavailable

GI For diagram(s), see printed CA Issue.

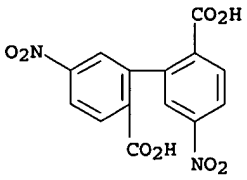
AB To confirm the conclusions that the photosensitizer forms an intermediate with the double role of dehydrogenating another mol. and adding mol. O, a phototropic diradical is sought whose free valence on O could be dehydrogenating, and on C add O. This must be preceded by the study of a diradical with 2 free O valences, then of one with 2 free C valences. 9,10-Phenanthrenequinone (I) should yield such a radical and react with SO2 as does a Cl atom (cf. Bonhoeffer, C.A. 17, 2392). A diagram of the app. shows the closed reaction vessel into which dips another closed, double-walled, H2O-cooled tube contg. the Hg vapor lamp. The soln. or suspension of o-quinone in C6H6 is satd. with SO2 before introduction into the reaction vessel. The photoreaction (no reaction in the dark) is formulated below. The hitherto unknown cyclic sulfuric acid esters, confirm the existence of intermediate phototropic diradicals. All these cyclosulfates are decompd. by heat to SO2 and the parent quinones. Wt. o-quinone, hrs. of illumination, wt. cyclosulfate formed, m.p., are : 25 g. I, 80, 28-30 g. (86-92%), 202-3.degree. (decompn.); 5 g. 3-nitro deriv. (II) of I, 53, 1.1 g. (17.5%), 190-1.degree. (decompn.); 5 g. 2-nitro deriv. (III) of I (cf. Schmidt and Spoun, C.A. 16, 3650), 60, 3 g. (48%), 204-6.degree. (decompn.); 1 g. 4-nitro deriv. (IV) of I, 20-5, 0.5 g. (40%), 185-6.degree. (decompn.); 30 g. tetrachloro-o-benzoquinone (V), 40, 25 g. (57%), 125-6.degree.; 12 g. o-naphthoquinone (VI), 200, 5.5 g. (33%), 73-4.degree.; 2 g. 3-nitro deriv. of VI, 20, 1.2-1.7 g. (45-65%), 143.degree.; 12 g. chrysoquinone (VII), 90-100, 12 g. (81%), 221-2.degree. (decompn.). The only previously reported compd. contg. C:C in a cyclosulfate ring is the intermediate product (VIII) in the prepn. of alizarinbordeaux (IX) from alizarin (X) with 75% oleum [cf. Schmidt, J. Prakt. Chem. 43, 239(1891)]. This prepn. was repeated to yield 1.6 g. (87%) VIII from 1.5 g. X, and its absorption max. (567 m.mu.) differed markedly from those of X (496 and 549 m.mu.) and IX (531 and 577 m.mu.), and from the hydrolysis and thermal decompn. products of VIII (same as IX). Analogous results from the cyclosulfate (XI) of II helped prove the course of the reaction for all cyclosulfates. Alk. hydrolysis of 3 g. XI gave 2.5-2.7 g. (59-63%) di-Na salt of the sulfuric acid half ester, (XII), with indicator properties, and acid hydrolysis of XII gave 3-nitro-9,10-dihydroxyphenanthrene, m. and mixed m.p. 221-3.degree. [cf. Schmidt and Kampf, Ber. 35, 3125(1902)]; Ac, deriv., m. and mixed m.p. 239-40.degree. (decompn.). Reduction of XI with Fe and glacial AcOH gave the corresponding unstable amino compd., m. 175-7.degree. (decompn.); Ac deriv., m. 198-213.degree. (decompn.). The cyclosulfate (XIII) of I and that of VI were stable toward both acid and alk. hydrolysis. Nitration of XIII resulted in XI (proved by thermal decompn. to the known II), or the 3,6-dinitro deriv. (XIV) of XIII, 55-60% yield, m. 240-1.degree. (decompn.). Thermal decompn. of XIV yielded SO2 and the 3,6-dinitro deriv. (XV) of I (73%), m. 293-6.degree. (from Ac2O) (decompn.); monoxime, m. 209-10.degree. (from glacial AcOH) (decompn.); quinoxaline (from o-phenylenediamine), m. 359-62.degree. (from C5H5N) (decompn.). XV was identified by bichromate oxidation to 5,5'-dinitrodiphenic acid, m. 286-8.degree.; Me ester, m. 160-1.degree.. Reduction of the cyclosulfate

of IV gave a compd. whose analysis agreed with the corresponding amino compd. with 1 mol. Me2CO, m. 172-3.degree. (from Me2CO-MeOH). The cyclosulfate of V reacted with PhNH2 to give a colorless, unidentified, S-free, N-contg. compd., m. 90-4.degree. (decompn.) (from CCl4). Reduction of the cyclosulfate of VI gave the corresponding amino deriv., m. 139-41.degree. (decompn.) (from dil. MeOH). Attempts to apply similar cyclosulfate synthesis to .alpha.-diketones and to p-quinones were unsuccessful. The evidence here given for the independent existence and exclusively photochemical formation of the phototropic diradicals with typical O-radical quality gives an exptl. soln. for the old problem of the valence tautomerism of quinones.

IT **92159-34-7**, Diphenic acid, 5,5'-dinitro-
(prepn. of)

RN 92159-34-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dinitro- (9CI) (CA INDEX NAME)



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L33 ANSWER 31 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1955:11903 CAPLUS

DN 49:11903

OREF 49:2382f-i,2383a-f

TI The relation between configuration and conjugation in biphenyl derivatives. III. The ultraviolet absorption spectra of some 2,2'-bridged compounds with m-substituents

AU Beaven, G. H.; Hall, D. Muriel; Lesslie, Mary S.; Turner, E. E.; Bird, Gwendoline R.

CS Univ. London

SO Journal of the Chemical Society, Abstracts (1954) 131-7
CODEN: JCSAAZ; ISSN: 0590-9791

DT Journal

LA Unavailable

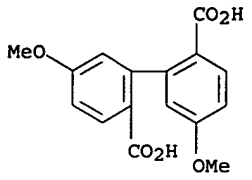
AB cf. C.A. 48, 1749i. The ultra-violet absorption spectra of the 2,2'-bridged biphenyls (I, II, III, R=H, R'=OMe) indicate that the m,m'-MeO groups reduce the conjugation across the 1,1'-bond by mesomeric interaction with the sep. benzene rings to which they are attached. This supports the view (C.A. 46, 11211e) that in noncoplanar biphenyls of this type there is still appreciable conjugation which is reduced by the introduction of either o,o'- or m,m'-MeO groups. Even in the o,o'-case, because of the noncoplanar configuration of the biphenyl skeleton, the effect of these substituents is not primarily steric. The spectrum of 2,2'-bitolyl was redetd.; this compd., in which there is some steric hindrance to free rotation, is still weakly conjugated. The conjugation is further diminished by the introduction of m,m'-MeO groups. The 2,2'-bridged biphenyls were prepd. thus: [2,5-Me(MeO)C6H3]2 (18 g.) added to a stirred, boiling KMnO4 soln. (48 g. in 2400 cc. H2O) contg. 0.5 g. MnSO4, then more KMnO4 after about 3 and 5 hrs. (12-g. portions, total heating time, 7-8 hrs., and the product pptd. with SO2 and purified through the Na salt, gave 55% [5,2-MeO(HO2C)C6H3]2, m. 228.degree.; di-Me ester (90%), m. 165-6.degree., reduced with LiAlH4 in Et2O, to 92% [5,2-MeO(HOCH2)C6H3]2 (IV), m. 107-8.degree.. IV melted under boiling H2O and treated with 50% H2SO4 gave 2,7-dihydro-2'',3'-dimethoxy-3,4,5,6-dibenzoxepin (II, R = H, R' = OMe), m. 159-60.degree.. IV (9 g.) added to 54 g. PBr3, gave 24.5 g. (92%) [2,5-BrCH2(MeO)C6H3]2 (V), m. 113-14.degree.. Adding 20 g. V to PhLi (from 1 g. Li and 10 g. PhBr) in 400 cc. warm Et2O, decompg. with H2O and a little HCl, sepg. the Et2O soln. and distg. gave I (R = H, R' = OMe), b1 205-15.degree., which solidified and when recrystd. from MeOH (4.6 g., 38%) and light petr. ether, m. 80-1.degree.; its soln. in alc. became yellow in sunlight and deposited crystals of 3,6-dimethoxyphenanthrenequinone, m. 235-6.degree.. Piperidine (9.5 g.) in C6H6 slowly added to 20 g. V in C6H6 reacted briskly and the quaternary bromide sepd. immediately; treated in H2O with KI soln. gave 2,7-dihydro-2''',3'-dimethoxy-3,4,5,6-dibenzazepinium-1-spiro-1''-piperidinium iodide, m. 274-5.degree. (from H2O). III, prepd. by shaking the iodide in water with AgBr, m. 270-1.degree.. From III, was prepd. the (+)-.alpha.-bromo-.pi.-camphorsulfonate (28.5 g.); crystn. from 3 l. C6H6 gave stout rhombohedrons, [.alpha.]5791 52.5.degree.,

[.alpha.]5461 62.5.degree. (EtOH), and sheaves of fine needles, [.alpha.]5791 45.9.degree., [.alpha.]5461 54.6.degree. (EtOH). Variations in rotation are explained by solvation. [2,5-(MeO2C)C6H3]2 reduced with a large excess of LiAlH4 in a Soxhlet app., H2O and HCl added, and the Et2O removed gave [2,5-(HOCH2)2C6H3]2 (VI), m. 202-3.degree.. Heated on a H2O bath 1 hr. with excess 2N H2SO4, VI gave in nearly quant. yield II (R = H, R' = CH2OH), m. 192.degree. (decompn.), converted to the bis(H phthalate), m. 179-9.5.degree. (aq. HOAc).

IT **6787-56-0**, Diphenic acid, 5,5'-dimethoxy-
(prepn. of)

RN 6787-56-0 CAPLUS

CN Diphenic acid, 5,5'-dimethoxy- (6CI, 7CI, 8CI) (CA INDEX NAME)



L33 ANSWER 32 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1949:10892 CAPLUS

DN 43:10892

OREF 43:2189g-i,2190a-c

TI p-Aminosalicylic acid

AU Justoni, R.; Terruzzi, M.; Pirola, C.

SO Farm. sci. e tec. (Pavia) (1948), 3, 509-25

DT Journal

LA Unavailable

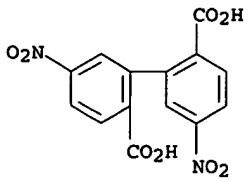
AB cf. C.A. 42, 7273c. The following steps were investigated to find the most practical method of manuf. 2,4-H2N(O2N)C6H3Me is acetylated with Ac2O giving 95% of the Ac compd. which, treated with KMnO4 in MgSO4 soln at 95.degree., gives 90% p-nitro-.omicron.-acetamidobenzoic acid, m. 215.degree., 225 g. of which, refluxed with HCl or H2SO4 in H2O, gives 180 g. 2,4-H2N(O2N)C6H3CO2H. Replacement of the NH2 with OH through the diazo compd. involves considerable loss by decarboxylation, which cannot be avoided by changing either concn., temp., or pH. Dinitrophenylacetic acid, m. 180.degree., is prepd. by treating 135 parts PhCH2CO2H with a mixt. of 1300 parts H2SO4 and 350 parts KNO3 below 60.degree.. The Me ester is prepd. from 180 parts acid with HCl in MeOH or, better, by adding H2SO4 contg. 20% SO3 in MeOH and partially evapg. in vacuo after 24 hrs. standing. Part of the ester crystallizes directly, part is obtained from the filtrate by adding NaOAc and evapn.; total yield 160 parts. The ester treated with iso-AmNO2 and iso-AmONa (Borsche, C.A. 6, 2422) forms 90% Me 6-nitro-3-indoxazenecarboxylate, and is then transformed into the nitrile (95%) of p-nitrosalicylic acid (I) by treating with NaOH. Sapon. with HCl gives 75, with H2SO4 83% I, purified through the Ba salt. The oxidation of 2,4-Cl(O2N)C6H3Me (II) to p - nitro - .omicron. - chlorobenzoic acid (III), m. 141-2.degree., is effected by adding a paste of II with (NH4)2Cr2O7 to H2SO4 at a temp. below 35.degree., heating finally to 55.degree., and mixing with ice; yield 63%. Oxidation of II with HNO3 gives 75% III. III is also prepd. in 75% yield from 2,4-H2N(O2N)C6H3CO2H through the diazo compd. 2,4-Cl(O2N)C6H3CN is prepd. in 50% yield from 2,4-Cl(O2N)C6H3NH2, through the diazo compd., with K2Ni(CN)4. Sapon. gives 80% III. I is prepd. from III with Ca(OH)2 and Cu salt or, better, with Ba(OH)2, but always with concomitant formation of 5,5'-dinitrodiphenic acid. Hydrolysis of III with p-MeC6H4SO3Na, CuOAc, and MgO at 170.degree. under pressure for 10 hrs. gives 76-7% I. I is reduced with Raney Ni at 70-80 atm. H pressure and 40.degree. in 66-72% yield, or as the Na salt in 10% aq. soln. at a pH 8 at 20 atm. 4 hrs. in 90% yield. By heating m-aminophenol 218 dissolved in KOH 112 and H2O 350 and mixed with K2CO3 690 in H2O 450 parts at 90.degree. under atm. CO2 pressure, 180 parts p-aminosalicylic acid is obtained.

IT **92159-34-7**, Diphenic acid, 5,5'-dinitro-
(prepn. of)

RN 92159-34-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dinitro- (9CI) (CA INDEX NAME)

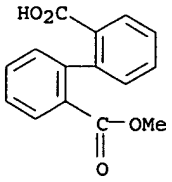
10082251



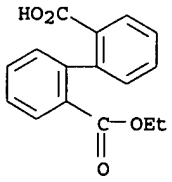
10082251

=> d l33 6,9,16,19,26,29 bib abs hitstr

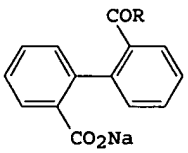
L33 ANSWER 6 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1989:496566 CAPLUS
DN 111:96566
TI Effect of structure on reactivity of aromatic derivatives. Part VII. Ionization constants of 2'-substituted biphenyl-2-carboxylic acids
AU Drapala, Tadeusz
CS Inst. Gen. Chem., Agric. Univ., Warsaw, 02528, Pol.
SO Polish Journal of Chemistry (1988), 62(4-6), 385-8
CODEN: PJCHDQ; ISSN: 0137-5083
DT Journal
LA English
AB Substituents R in o-(o-RC6H4)C6H4CO2H (I; R is, e.g., NO2, OMe) lower the activity of the carboxyl group relative to I (R = H), irresp. of their Hammett .sigma.'s.
IT **6926-84-7**, 2'-Methoxycarbonyl-2-biphenylcarboxylic acid
27428-70-2, 2'-Ethoxycarbonyl-2-biphenylcarboxylic acid
RL: PRP (Properties)
(ionization const. of)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



RN 27428-70-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monoethyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 9 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1987:119178 CAPLUS
DN 106:119178
TI High-resolution proton NMR study of diphenic acids
AU Gu, Ruilin; Li, Zhenghua
CS Pharmacol. Dep., West-China Med. Univ., Peop. Rep. China
SO Bopuxue Zazhi (1986), 3(2), 105-11
CODEN: BOZAE2; ISSN: 1000-4556
DT Journal
LA Chinese
GI

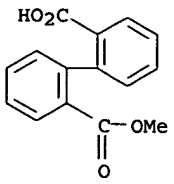


I

AB High-resoln. 1H-NMR spectra of eight typical diphenic acids e.g., I (R = MeO, NH2) were reported. The chem. shifts of complex system of biphenyl

protons can be identified by the double resonance method, but cannot be detd. in 80 MHz 1H-NMR spectra.

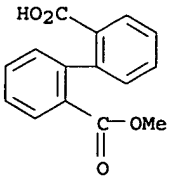
IT 107106-75-2
RL: PRP (Properties)
(NMR spectra of)
RN 107106-75-2 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester, sodium salt (9CI) (CA INDEX NAME)



Na

L33 ANSWER 16 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1974:551921 CAPLUS
DN 81:151921
TI Studies on the Hurtley reaction
AU Cirigottis, Kerrie A.; Ritchie, E.; Taylor, W. C.
CS Dep. Org. Chem., Univ. Sydney, Sydney, Australia
SO Australian Journal of Chemistry (1974), 27(10), 2209-28
CODEN: AJCHAS; ISSN: 0004-9425
DT Journal
LA English
AB For the Hurtley reaction the best and most convenient solvents is EtOH; the reaction succeeds best with arom. 0-bromocarboxylic acids although 0-iodo acids give low yields; replacement of the carboxy group by any other functional group prevents the reaction; a Cu species, probably Cu(I), is an essential catalyst. The reactivity of 8-bromo-1-naphthoic acid, which is almost identical with that of 0-bromobenzoic acid, is evidence against the intermediacy of a planar resonance hybrid structure. The geometry of the bromo acid-copper intermediate appears to be of paramount importance.

IT 6926-84-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(reaction of, with thallium ethoxide)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 19 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1971:476591 CAPLUS
DN 75:76591
TI Syntheses of benzoheterocyclic compounds. VI. Diphenide and its methoxyl derivatives
AU Kobayashi, Shigeru; Senoo, Fusako; Kihara; Masaru; Sakata, Kikuko; Miura, Akira
CS Pharm. Fac., Univ. Tokushima, Tokushima, Japan
SO Chemical & Pharmaceutical Bulletin (1971), 19(6), 1262-7
CODEN: CPBTAL; ISSN: 0009-2363
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB Diphenides I (R-R2 = H, OMe) were prepd. in 50-77% yield by intramol. Cannizzaro reaction of o-HOCC6H4C6H4CHO-o or its methoxylated derivs.

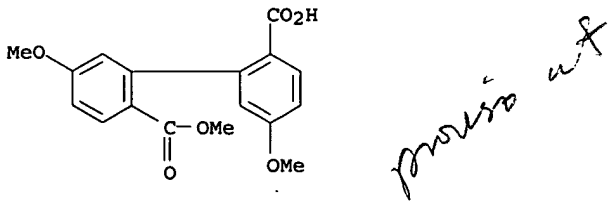
10082251

Partial redn. of the correspondingly substituted diphenic acids with NaBH4 gave 56-87% I. I (R = R1 = H, R2 = OMe) could not be prepd. by the latter reaction.

IT 33200-36-1P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

RN 33200-36-1 CAPLUS

CN Diphenic acid, 5,5'-dimethoxy-, monomethyl ester (8CI) (CA INDEX NAME)



L33 ANSWER 26 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1959:34694 CAPLUS

DN 53:34694

OREF 53:6185c-i,6186a-i,6187a-b

TI Chloromethylation of 3,3'-dimethoxybiphenyl and of 3,3',4,4'-tetramethoxybiphenyl. Synthesis of derivatives of 2,3,6,7-tetramethoxyphenanthrene, of 2,3,9,10-tetramethoxydibenzo(a,c)cycloheptadiene, and of 2,3,6,7-tetramethoxyfluorene

AU Matarasso - Tchiroukhine, Elisabeth

CS Univ. Paris

SO Ann. Chim. (Paris) (1958), 3(13), 405-59

DT Journal

LA Unavailable

AB m-Aminophenol was converted to m-bromophenol, b12 112.degree., m. 33-4.degree., by a Sandmeyer reaction, and treated with Me2SO4 to give m-bromoanisole (I), b11-12 95.degree.. I was converted to the Grignard reagent, and thence in 40% to 3,3'-dimethoxybiphenyl (II), b0.8 148.degree., m. 35-6.degree., either by anhyd. FeCl3 (method of Champetier, C.A. 25, 1752), or by CoCl2 (method of Kharasch and Fields, C.A. 35, 73682, in 30% yield, more violent reaction)in C4H8O. II (11 g.) was treated with 43 cc. MeOCH2Cl in 100 cc. HOAc (with 0.2% Ac2O) 5 hrs. at 50.degree. and cooled. Addn. of ice H2O caused formation of a viscous paste which was immediately extd. with C6H6. The C6H6 soln. was washed with H2O (base caused resinification) to remove acid, dried quickly over Na2SO4, and distd. to give 40% 2,2'-bis(chloromethyl)-5,5'-dimethoxybiphenyl (III), b1 180-2.degree., m. 79-80.degree. (C6H12), n 1.608. A kinetic study indicated the reaction rate to be independent of concn. of reagents. III (8.6 g.) with 1 g. LiAlH4 and 0.9 g. LiH in anhyd. C4H8O at reflux 2 hrs. 30 min. then at room temp. 15 hrs. with decompn. of the complex in H2SO4 gave 40% 2,2'-dimethyl-5,5'-dimethoxybiphenyl (IV), b3 142-7.degree., m. 49.degree. (HOAc-H2O). IV was oxidized with 2% KMnO4 to 10% 5,5'-dimethoxybiphenyl-2,2'-dicarboxylic acid, m. 222-4.degree.. 1-Bromo-3,4-dimethoxybenzene, b13-14 140.degree., was prepd. in 50-60% yield by bromination of catechol di-Me ether in HOAc and converted to 3,3',4,4'-tetramethoxybiphenyl (V), m. 133-4.degree. (MeOH), by treatment of the Grignard reagent with FeCl3 (35% yield) or CoCl2 (40-50% yield). V (13.2 g.) in 300 cc. anhyd. dioxane satd. with HCl was treated with 22 cc. 30% aq. HCHO 30 min. at 0.degree., then overnight at room temp. Purification similar to that for III gave 80% 2,2'-bis(chloromethyl)-4,4',5,5'-tetramethoxybiphenyl (VI), m. 161.degree. (C6H6). VI (11 g.) in 140 cc. HOAc and 30 cc. H2O refluxed 2 hrs. gave 70% 2,3,9,10-tetramethoxy-5,7-dihydrodibenz-[c,e]oxepine (VII), m. 256.degree. (C6H6). LiAlH4 treatment similar to that for IV gave 80% 2,2'-dimethyl-4,4',5,5'-tetramethoxybiphenyl (VIII), m. 117.degree. (MeOH). Ultraviolet spectra were obtained for CHCl3 solns. of III, VI, VII, and VIII, and comparisons made. Condensation of 1.24 g. VI with 1 g. (CH2)6N4 in 11 cc. anhyd. CHCl3 gave 80% salt, m. 220.degree. (decompn.), 0.5 g. of which was hydrolyzed at reflux 1 hr. in 5 cc. 1:1 HOAc-H2O to give traces of a carbonyl compd. (aldehyde?), m. about 200.degree.. VI (1.7 g.) in 50 cc. HOAc was treated with 1.8 g. AgOAc to give 15% diacetate (IX) of 2,2'-bis(hydroxymethyl)-4,4',5,5'-tetramethoxybiphenyl, m. 99-100.degree. (MeOH). VI (1 g.) with 0.2 g. NaOEt gave 70-80% 2,2'-bis(ethoxymethyl)-4,4',5,5'-tetramethoxybiphenyl (X), m. 74-5.degree. (Et2O). To 4 g. VI in 160 cc. Me2CO was added slowly 1.7 g. KCN in 10 cc. EtOH-4 cc. H2O; after 2 hrs. reflux the solvent was reduced to 0.25 vol., cooled, and treated with H2O to ppt. 60% 2,2'-bis(cyanomethyl)-4,4',5,5'-tetramethoxybiphenyl (XI), m. 145.degree. (EtOH). XI (0.95 g.) was

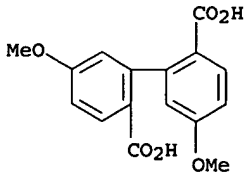
treated with 10 cc. Ac2O at 10.degree. a week then with a little aq. NH4OH to give 60% 2,2'-bis(carbamoylmethyl)-4,4',5,5'-tetramethoxybiphenyl, m. 237-8.degree. (MeOH). Thorpe condensation of XI with KOH or NaOEt in EtOH gave 85-100% 5-cyano-2,3,9,10 - tetramethoxy - 6 - iminodibenzo[a,c]cycloheptadiene (XII), m. 242.degree. (EtOH). VII (4.6 g.) in 30 cc. H2O and 280 cc. HOAc was refluxed 3 hrs. with 4 g. K2Cr2O7, cooled, and treated with much H2O to give 60% 2,2'-diformyl-4,4',5,5'-tetramethoxybiphenyl (XIII), m. 215.degree. (xylene); dioxime, m. 295-6.degree. (MeOH); bis(phenylhydrazone), m. 263-4.degree. (Et2O). XIII is remarkably resistant to KMnO4 oxidation, but 3 g. XIII with 30 g. Na2Cr2O7 in 100 cc. HOAc refluxed 1 hr. gives 2,3,6,7-tetramethoxyphenanthrene-9,10-quinone-H2O (XIV), m. 262.degree.; quinoxaline deriv., m. 276.degree. (HOAc). XIII does not undergo benzoin condensation or Cannizzaro reaction. Reduction of 1 g. XIII in C4H8O with 0.4 g. LiAlH4 and 0.4 g. LiH gave on ice H2O-H2SO4 treatment 2,2'-bis(hydroxymethyl) - 4,4',5,5'- tetramethoxybiphenyl-0.5H2O (XV), m. 128.degree. (m. 136-7.degree. after heating to 129.degree.). XV with Ac2O gave IX, m. 99-100.degree., and with H2SO4 gave VII. Since VI gave resins with Na, Cu, and Zn, and did not react with Mg, 2,3,6,7-tetramethoxy-9,10-dihydrophenanthrene (XVI) was prepd. from 2,2'-bis-(bromomethyl)-4,4',5,5'-tetramethoxybiphenyl (XVII), m. 183-4.degree. (PhMe), obtained in 50% yield from XV with PBr3. To 1.1 g. XVII in 50 cc. C4H8O under N PhLi (from 15 cc. PhBr and 1.2 g. Li in 15 cc. Et2O) was slowly added at room temp., cooled, ice H2O added, and extd. with CHCl3 giving 98% XVI, m. 178-9.degree. (CHCl3); picrate, m. 132-3.degree. (MeOH). XVI in Tetralin with Pd-C gave 2,3,6,7-tetramethoxyphenanthrene (XVIII), m. 206-8.degree. (MeOH); picrate, m. 206-8.degree. (MeOH). LiAlH4 treatment of XIV gave 50-60% 2,3,6,7-tetramethoxy - 9,10 - dihydro - 9,10 - dihydroxyphenanthrene, m. 202-3.degree. (C6H6); diacetate, m. 205-6.degree. (MeOH), but refreezes and rem. 215-17.degree.; picrate of diacetate, m. 198-200.degree. (MeOH). XII (2.2 g.) was added slowly to 30 cc. cold concd. H2SO4, kept at room temp. 20 hrs., neutralized, and extd. giving 70% 2,3,9,10-tetramethoxy-6-iminodibenzo[a,c]cycloheptadiene-5-carboxylic acid, m. 217-18.degree. (CHCl3), which on refluxing 2 hrs. in dil. HCl gave 50-60% 2,3,9,10-tetramethoxydibenzo[a,c]-6-cycloheptadienone (XIX), m. 259.degree. (HOAc); oxime, m. 189.degree. (EtOH). XIX (0.15 g.) refluxed 3 hrs. in 5 cc. Ac2O with 0.10 g. SeO2 gave 30% XIV, m. 262.degree.; no tropolone was isolated. Treating 21 g. VI in 420 cc. anhyd. C4H8O with a soln. prepd. from 9.6 g. CH2(CO2Et)2 in 140 cc. C4H8O and 2.8 g. Na in 36 cc. abs. EtOH, refluxing 2-3 hrs., keeping overnight, treating with ice H2O, and extg. with CHCl3 gave 60% di-Et 2,3,9,10-tetramethoxydibenzo[a,c]cycloheptadiene-6,6-dicarboxylate (XX), m. 126.degree., sapon. no. 242. On sapon. with alc. KOH, XX gave 100% dicarboxylic acid, m. 236-7.degree., which on heating to 160-70.degree. decarboxylated to 70-80% 2,3,9,10-tetramethoxydibenzol[a,c]cycloheptadiene - 6 - carboxylic acid (XXI), m. 214-15.degree. (xylene); Et ester, m. 158-9.degree. (EtOH); hydrazide, m. 186-7.degree. (EtOH); semicarbazide, m. 244-5.degree. (EtOAc). Hydrazide of XXI (1.6 g.) in 500 cc. H2O contg. 2.5 cc. concd. HCl was treated with 0.4 g. NaNO2 in 22 cc. H2O 30 min. at 0.degree. giving azide (XXII). XXII refluxed 4 hrs. with 100 cc. abs. EtOH and concd. to 20 cc. gave 50% XXI ethylcarbamate, m. 134.degree. (EtOH or PhMe). XXII (again from 1.6 g. hydrazide) on heating 3-4 hrs. in C6H6 gave the isocyanate, which was treated with LiAlH4 and LiH in C4H8O to give 65% 6-(N-methylamino)-2,3,9,10-tetramethoxydibenzo[a,c,]cyclohepta diene (XXIII), m. 228.degree. (C6H6); 2 picrates, one m. 278.degree. (decompn.) (MeOH); benzenesulfonamide, m. 231-2.degree. (C6H6). Crude XXIII (1 g.), 2.1 g. HCO2H, and 1 g. 30% aq. HCHO was refluxed 17 hrs., cooled, poured into H2O, extd. with C6H6, and dried to give 80% 6 - (N,N - dimethylamino) - 2,3,9,10 - tetramethoxydibenzo[a,c]cycloheptadiene (XXIV), m. 113-14.degree. (Et2O); picrate, m. 260-1.degree. (EtOH). Crude XXIV (0.4 g.) refluxed 1 hr. in 1 cc. MeOH with 0.4 g. MeI gave the quaternary iodide (XXV), m. 320.degree. (decompn.), which refluxed 3 hrs. with 1 g. Na in 50 cc. abs. EtOH, concd., cooled, and extd. gave 90% 2,3,9,10-tetramethoxydibenzo[a,c]cycloheptatriene, m. 158-9.degree. (C6H6), resolidified m. 166-7.degree.. V (2.7 g.) in 10 cc. HOAc (0.2% Ac2O) with 1.5 cc. ClCH2CH(OEt)2 at 5.degree. was treated with 10 cc. H2SO4 in 10 cc. HOAc 2 hrs. at 5-10.degree. and 20 hrs. at room temp. to give 80% 9-chloromethyl-2,3,6,7-tetramethoxyfluorene (XXVI), m. 206.degree. (EtOH). 9-Bromomethyl-2,3,6,7-tetramethoxyfluorene, m. 206.degree., was obtained in 80% yield similarly. Dehydrohalogenation of XXVI with alc. KOH gave a quant. yield of 9-methylene-2,3,6,7-tetramethoxyfluorene (XXVII), m. 201.degree. (EtOH), rapidly decolorized Br soln. Pyridine or thermal dehydrohalogenation at 206.degree. gave the same product. XXVII with KMnO4 gave 2,3,6,7-tetramethoxyfluorenone, m. 203.degree. (EtOH). V (9.4 g.) in 30 cc. HOAc with 6 cc. H2NCH2CH(OEt)2 at 5.degree. was treated with 30 cc. H2SO4 and 30 cc. HOAc 3 hrs. at 5-10.degree. and 20 hrs. at room temp. to give 65% 9-(aminomethyl)-2,3,6,7-tetramethoxyfluorene (XXVIII), m. 215-16.degree. (C6H6); hydrochloride,

decomp. 220.degree.; acetanilide, m. 181.degree. (EtOH); picrate, m. 275.degree. (decompn.) (EtOH). NaNO2 treatment of the XXVIII.HCl gave traces of XXVII; isoamyl nitrite on XXVIII gave traces of XXVI and resinous products when treated with HCl during workup.

IT **6787-56-0**, Diphenic acid, 5,5'-dimethoxy-
(prepn. of)

RN 6787-56-0 CAPLUS

CN Diphenic acid, 5,5'-dimethoxy- (6CI, 7CI, 8CI) (CA INDEX NAME)



L33 ANSWER 29 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1955:56586 CAPLUS

DN 49:56586

OREF 49:10886d-g

TI Tuberculostatic activity of some derivatives of p-aminobenzoic acid

AU van der Stelt, C.; Voorspuij, A. J. Zwart; Nauta, W. Th.

CS Amsterdam Univ. Hosp.

SO Antonie van Leeuwenhoek (1954), 20, 285-98
CODEN: ALJMAO; ISSN: 0003-6072

DT Journal

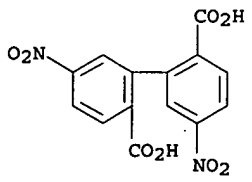
LA Unavailable

AB The following compds. were tested: 4-nitrobenzoic acid (I) and its Me, Et, Pr, iso-Pr, cyclopentyl, 1,3-di-methylbutyl, 2-ethylbutyl, 1-methylhexyl, 2-ethylhexyl, 2,6-dimethyl-4-heptyl, 3,5,5-trimethylhexyl, and 3,5,5-trimethylcyclohexyl esters, I hydrazide, 3-methyl-4-nitrobenzoic acid, 4-nitroisophthalic acid, 4-nitrophenylacetic acid (II) and its Me and Et esters, 5-nitro-2-furoate, Me 5-nitro-2-thiophenecarboxylate, Me 4-amino-3,5-dichlorobenzoate, 3,3'-diamino-5,5'-dicarboxydiphenyl, the Me and Pr esters and the hydrazide of 4-H2NC6H4CO2H (IIa), (4-H2NC6H4CO)2, (4-AcNHC6H4CO)2, 4,4'-diacetylaminobenzoin, (4-H2NC6H4)2CO, (4-AcNHC6H4)2CO, (4-H2NC6H4)2CH2, 4-AcNHC6H4CHO, "4-(benzoyl-thioureido)benzoic acid," 4-aminophenylacetic acid (IIb), Et ester of IIb, hexahydrobenzoic acid lactam (sic), 2-amino-5-carboxypyridine, Et 5-amino-2-furoate, Et 5-amino-2-thiazolecarboxylate, and the following IIa (substituents given): 3-Me; 3,5-di-Me; 3-Cl; N-Ac, 3-Cl; 3-Br; 3,5-di-Br; 3-I; 3-O2N; N-Ac, 3-H2N (III); 3-HO2C; 2-Me; 2,6-di-Ph; 2-Cl; 2-Br; 2-I; N-Ac, 2-I; 2-H2N; 2-HO; 2-HS; 2-HO2C; N,N-di-Me; N-Bu; N-n-hexyl (IV); N-PhCH2; N-benzal; N-Ac; N-Bz; N-ClCH2CO; N-Cl2CHCO; N-EtO2C; N-H2NC(:O); N-H2NC(:S) (V); N-H2N; N-Me, N-ON. The syntheses of III, IV, 5,5'-dinitrodiphenic acid, and of esters of I are described. Some of these esters showed activity on Youmans medium but not on the protein-contg. Beewkes medium. V m. above 330.degree..

IT **92159-34-7**, Diphenic acid, 5,5'-dinitro-
(prepn. of)

RN 92159-34-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dinitro- (9CI) (CA INDEX NAME)



=> d l33, 8, 18, 28 bib abs hitstr

L33 ANSWER 8 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

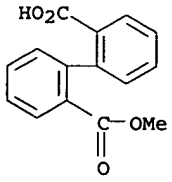
AN 1989:23217 CAPLUS

DN 110:23217

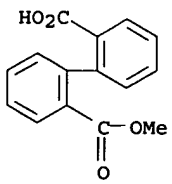
TI Dissociation of the derivatives of benzoic acid in the mixed media

10082251

AU Foltin, M.; Zuffova, H.; Benko, J.
CS Fac. Nat. Sci., Komensky Univ., Bratislava, 842 15, Czech.
SO Acta Facultatis Rerum Naturalium Universitatis Comenianae, Chimia (1987), Volume Date 1986, 34, 129-39
CODEN: AFRCAQ; ISSN: 0524-2312
DT Journal
LA English
AB Relative values of the half-neutralization potential (HNP) were detd. for BzOH and 12 of its derivs. as a function of cosolvent mole fraction in H2O-Me2CO and H2O-DMF mixts. The HNP values are reproducible and exptl. accessible. The effect of solvent structure can be examd. from the above dependence. The differentiating ability of H2O-Me2CO was better than that of H2O-MeOH, whereas that of H2O-DMF was worse.
IT **6926-84-7**, Monomethyl diphenate
RL: PROC (Process)
(ionization of, solvent effect on)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 18 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1973:526554 CAPLUS
DN 79:126554
TI Selective reduction of aromatic carboxyl groups to methyl in the presence of ester functionality. Potentially new procedure for the preparation of ester-containing organosilanes
AU Benkeser, R. A.; Ehler, D. F.
CS Dep. Chem., Purdue Univ., West Lafayette, IN, USA
SO Journal of Organic Chemistry (1973), 38(20), 3660
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
AB The carboxyl groups of a representative series of aromatic half esters were reduced to Me by Cl3SiH-Pr3N. The ester functionality was not reduced but was sapond. by the base employed to cleave the intermediate benzylic silanes. In the case of p-[EtOC(O)]C6H4CO2H, the intermediate p-[EtOC(O)]C6H4CH2SiCl3 was isolated and characterized. Treatment of the latter with a slight excess of base caused benzyl Si-C cleavage but no sapon. and p-ethyl toluate was obtained.
IT **6926-84-7**
RL: RCT (Reactant); RACT (Reactant or reagent)
(selective carboxyl redn. of)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



L33 ANSWER 28 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1956:1405 CAPLUS
DN 50:1405
OREF 50:281g-i,282a-h
TI Coal-tar anthracene oil
AU Kruber, Otto; Raeithel, Armin
CS Ges. Teerverwert. m. b. H., Duisburg-Meidrich, Germany
SO Chemische Berichte (1954), 87, 1469-78

10082251

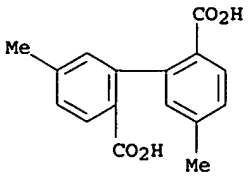
CODEN: CHBEAM; ISSN: 0009-2940
DT Journal
LA Unavailable
AB The following new components were found in coal tar anthracene oil: 1-methylfluorene (I), diphenylsuccindan (C.A. 4b,5,9b,10-tetrahydroindeno[2,1-a]indene) (II), 2-methylphenanthrene (III), 3,6-dimethylphenanthrene (IV), and 1,8-dimethylbiphenylene sulfide (V) of which V was unknown. I was obtained from the anthracene oil fraction, b. 316.5-18.degree. (cf. C.A. 47, 1701d) by fractional distn., freezing out, and Na fusion. The unreacted oil was sulfonated at room temp. with 10% by wt. portions of 92% H2SO4 (2 times), 95% (4 times), and 97% (to completion). The crude cryst. sulfonic acids obtained upon cooling from sulfonation fractions 3-7 were desulfonated with 50% H2SO4. Distg. up to 115.degree. gave a noncrystg. oil, from 115-30.degree. an oil which partly crystd. upon cooling to give I, white needles from MeOH, m. 86-7.degree. (identified by oxidation to 1-methylfluorenone, yellow needles from petroleum ether, m. 98-9.degree.) and fluorenone-1-carboxylic acid, yellow needles by sublimation, m. 195-6.degree.. II was obtained from the anthracene oil fraction, b. 333-5.degree. (C.A. 49, 7575a). Fractions 8-14 of the yellow oil (loc. cit.) (640 g.) were treated with 50 g. of 100% H2SO4 in presence of Ac2O at 15.degree., the unreacted oil (485 g.) was agitated with 160 g. 100% H2SO4 for 3 hrs. at 70.degree.. The sulfonic acid layer was repeatedly extd. with benzene, and the combined ext. and unsulfonated oil, after washing to neutrality and evapg. the benzene, was distd. in vacuo. After sepg. 55 g. biphenylene sulfide crystg. from 285 g. distillate, the remaining 181 g. oil was again treated with 150 g. 100% H2SO4 at 70-5.degree., the sulfonated product worked up as above gave 20.5 g. of a dark oil from which crystd. 6.6 g. of crude II (4.7 g. of white needles from EtOH, m. 104-4.5.degree.), identified by the mixed m.p. with the synthetic product [cf. Ann. 247, 157(1888)]. The ultraviolet spectrum of II in EtOH closely resembles that of hydrindene. III was isolated from the heavy ends of the anthracene oil fraction, b. 350-70.degree., which was dissolved in an equal amount of PhMe. The filtrate, after evapg. the solvent, was fused with KOH to remove carbazoles, extd. with dil. acid then alkali to remove bases and phenols, resp., and treated with Na at 190-200.degree. to remove most of the 4,5-methylene-phenanthrene. From the remaining oil a 3.5 kg. fraction, b. 350-60.degree., was redistd. at 30 mm. Hg in an adiabatic column of about 28 theoretical plates at a reflux ratio of 30:1 to fractions of 100 g. each. The cryst. portion of fractions 11-16 was distd. over Na and recrystd. from EtOH to give 150 g. III, colorless leaflets, m. 56.degree., b760 354.8.degree.. III was further purified by dissolving in a little PhMe and sulfonated at 40-5.degree. with concd. H2SO4, recrystd. from 33% H2SO4, and desulfonated with 33% H2SO4 at 125-30.degree. to give III, m. 57-7.5.degree.; picrate, orange needles, m. 120-1.degree.. Oxidation of III gave 2-methylphenanthrenequinone (VI), orange leaflets, m. 155-6.degree.; condensation of VI with o-C6H4(NH2)2 gave the corresponding quinoxaline, pale yellow needles, m. 196-7.degree.. The soln. obtained upon treating 2 g. VI with 10 cc. 30% H2O2 and 18 cc. of 2N NaOH at room temp. for 1.5 hrs., when dild. with H2O, kept overnight, and filtered gave upon acidification of the filtrate 4-methyldiphenic acid, colorless needles from very dil. EtOH, m. 246-7.degree.. The latter can be obtained directly from III by refluxing with 30% H2O2 in AcOH for 2.5 hrs. and converted to 2-methylfluorenone by dry distn. over CaO. IV was obtained from the heavy ends of the anthracene oil fraction, b. 355-60.degree., after pretreatment as described for the prepn. of III, by distg. 7 kg. in an adiabatic column of about 18 theoretical plates at a reflux ratio of 20:1 at 30 mm. Hg to fractions of about 120 g. each. Fractions 6-10, upon redistn., served as starting material for the isolation of V. The 4 penultimate fractions obtained upon redistn. of fractions 20-32 in the same column gave 45 g. IV, colorless needles, m. 141.degree. (from EtOH), b760 363.2.degree.; picrate, orange needles, m. 172-3.degree.; oxidation gave 3,6-dimethylphenanthrenequinone, orange needles, m. 221-2.degree. (from EtOH), which condensed with o-C6H4(NH2)2 to the corresponding quinoxaline, pale yellow needles, m. 266-7.degree. (from EtOH). Heating 4 g. IV in 30 cc. of AcOH to boiling and gradually adding 24 cc. 30% H2O2 gave 2.2 g. 5,5'-dimethyldiphenic acid, pale yellow leaflets, m. 268-70.degree. (from H2O) which upon dry distn. with CaO gave 3,6-dimethylfluorenone, orange leaflets, m. 116-17.degree. (from petroleum ether). The filtrate obtained from the above mentioned crude starting material for V was sulfonated with 92% H2SO4 at room temp., and the unsulfonated oil adsorbed on Al2O3 and eluted first with petroleum benzin and then with a mixt. of benzene and EtOH. The colorless oily eluate, nD20 1.669, crystd. on standing V, white needles, m. 154-5.degree. (from EtOH); picrate, yellow needles, m. 130-1.degree.. Heating 0.2 g. V in 5 cc. of glacial AcOH with 0.5 cc. 30% H2O2 on the waterbath gave 0.2 g. 1,8-dimethyldiphenylenesulfone, white needles, m. 293-4.degree. (from EtOH or glacial AcOH), heating 10 g. 2,2'-dihydroxy-3,3'-dimethylbiphenyl with

5 g. P2S5 in an Anschutz distn. flask over 15 min. from 140 to 410.degree. gives 0.38 g. V after recrystg. the crude distillate from EtOH.

IT **93012-36-3**, Diphenic acid, 5,5'-dimethyl-
(prepn. of)

RN 93012-36-3 CAPLUS

CN Diphenic acid, 5,5'-dimethyl- (7CI) (CA INDEX NAME)



=> d l33, 7, 17, 27 bib abs hitstr

L33 ANSWER 7 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1989:173045 CAPLUS

DN 110:173045

TI Potential antitumor agents. 58. Synthesis and structure-activity relationships of substituted xanthenone-4-acetic acids active against the colon 38 tumor in vivo

AU Rewcastle, Gordon W.; Atwell, Graham J.; Baguley, Bruce C.; Calveley, Stephen B.; Denny, William A.

CS Sch. Med., Univ. Auckland, Auckland, N. Z.

SO Journal of Medicinal Chemistry (1989), 32(4), 793-9
CODEN: JMCMAR; ISSN: 0022-2623

DT Journal

LA English

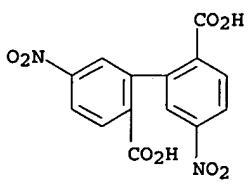
OS CASREACT 110:173045

AB A series of Me-, MeO-, Cl-, O2N-, and HO-substituted oxoxantheneacetic acids were prepd. and evaluated against s.c. implanted colon adenocarcinoma 38 in vivo, by using a short-term histol. assay as a primary screening system. E.g., condensation of 2,4-Cl2C6H3CO2Na and 2-MeC6H4ONa in the presence of CuCl and (MeOCH2CH2OCH2CH2)3N gave 4,2-Cl(2-MeC6H4O)C6H3CO2H. The latter was oxidized in polyphosphate ester to give 6-chloro-4-methyl-9-xanthenone, which was converted in several steps to 6-chloro-9-oxoxanthene-4-acetic acid. The level of activity of the compds. prepd. depended more on the nature of the substituent than its positioning, in the order: Cl > Me, OMe > NO2, OH. However, the potency of the compds. was related much more to the position rather than the nature of the substitution, with 5-substituted compds. being clearly the most potent. 5-Methyl-9-oxoxanthene-4-acetic acid has a similar level of activity to that of flavoneacetic acid in the test systems employed but is more than 7-fold as dose potent.

IT **92159-34-7P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

RN 92159-34-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, 5,5'-dinitro- (9CI) (CA INDEX NAME)



L33 ANSWER 17 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN

AN 1974:535645 CAPLUS

DN 81:135645

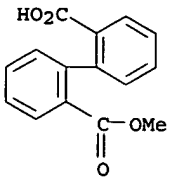
TI Selective reduction of aromatic carboxyl groups to methyl in the presence of ester functionality. Potentially new procedure for the preparation of ester-containing organosilanes

AU Benkeser, R. A.; Ehler, D. F.

CS Dep. Chem., Purdue Univ., West Lafayette, IN, USA

10082251

SO Journal of Organic Chemistry (1973), 38(20), 3660
CODEN: JOCEAH; ISSN: 0022-3263
DT Journal
LA English
AB The carboxyl groups of a representative series of aromatic half esters were reduced to Me by Cl3SiH-Pr3N. The ester functionality was not reduced but was sapond. by the base employed to cleave the intermediate benzylic silanes. In the case of p-[EtOC(O)]C6H4CO2H, the intermediate p-[EtOC(O)]C6H4CH2SiCl3 was isolated and characterized. Treatment of the latter with a slight excess of base caused benzyl Si-C cleavage but no sapon. and p-Et toluate was obtained.
IT 6926-84-7
RL: RCT (Reactant); RACT (Reactant or reagent)
(selective redn. of the carboxyl group)
RN 6926-84-7 CAPLUS
CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



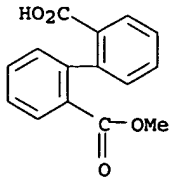
L33 ANSWER 27 OF 32 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1957:29789 CAPLUS
DN 51:29789
OREF 51:5735g-i,5736a-d
TI Attempted synthesis of 2,3-dihydrodibenz[d,f]azepin-3-one
AU Muth, Chester W.; Sung, Wei-Lang
CS West Virginia Univ., Morgantown
SO West Va. Univ. Bull. (1955), Ser. 56(No. 12-15), 46-9
DT Journal
LA Unavailable
AB cf. C.A. 50, 1766e. Excess CH2N2 in Et2O was added to 5.0 g. 2,2'-diphenamic acid (I), the mixt. kept overnight and concd. and the residue crystd. from C6H6-petr. ether yielding 4.4 g. 2'-carbamoyl-2-carbomethoxybiphenyl (II), white crystals, m. 96-7.degree., also prepd. but only in 50% yield by heating I 2.5 hrs. with MeOH satd. with HCl, in 40% yield by treating NH4OH with the acid chloride of 2'-carbomethoxy-2-biphenylcarboxylic acid. To MeONa, prepd. from 1.4 g. Na and 60 ml. MeOH, was added 3.61 g. Br in 5 ml. MeOH and 5 g. II in 10 ml. MeOH, the temp. maintained 10 hrs. below 15.degree. the mixt. then heated 15 min. at 70-90.degree., cooled, neutralized with 6N HCl, 2/3 of the solvent removed by distn., the residue poured into 300 ml. H2O, and the resulting solid filtered off and washed with 25 ml. boiling H2O, and crystd. from C2H2 yielding 0.34 g. fine white crystals, m. 217-18.degree.. After standing overnight the filtrate yielded 3.56 g. unchanged II. Four addnl. attempts were made with reflux periods of 10 to 30 min., and molar ratios of II, Br, and MeONa of 1:0.55:2.5 to 1:9.5:17.0. To freshly prepd. MeONa, from 0.14 g. Na in 20 mt. MeOH, was added 0.5 g. II in 10 ml. MeOH at 15.degree., the mixt. heated 15 min., cooled, neutralized with concd. HCl, 1/2 of the solvent removed by distn., the residue cooled and poured into 50 ml. cold H2O, and the resulting needles sepd. and dried yielding 0.44 g. 2,2'-diphenimide, m. 217-19.degree.. 3,5-Dichloro-2-aminobiphenyl-HCl (III) (15.0 g.), 7.7 g. BrCH2CO2H, and 8.82 g. NaOH in 90 ml. H2O was refluxed 18 hrs., cooled, extd. with Et2O, and the Et2O layer dried and concd. to give a dark, viscous mass which was crystd. from MeOH yielding 4.5 g. unchanged III. III (9.35 g.) and 4.70 g. BrCH(CO2Et)2 was heated 5 hrs. on a steam bath, 40 ml. 30% NaOH in MeOH added, heating continued 3 hrs., a portion of MeOH distd., the residue shaken with 30 ml. Et2O and 50 ml. H2O, and the aq. layer carefully acidified with 6N HCl, again yielding no oil or ppt. III (6.35 g.) in 25 ml. anhyd. C6H6, was added dropwise to 20 ml. (COCl)2 at 70-80.degree., the mixt. concd., the residue stirred with excess dil. NaOH, and 1.96 g. light brown solid filtered off, and crystd. from C6H6, PhNO2, and C6H4Me2 to give N,N'-bis(3,5-dichloro-2-biphenylyl)oxamide (IV), m. 229-30.5.degree.. When the alk. filtrate from IV was made acidic with HCl, a ppt. of 3.36 g. N-(3,5-dichloro-2-biphenylyl)oxamic acid (V), m. 173-6.degree., was formed. An attempted ring closure was made by heating 2.06 g. V and 12.5 ml. SOCl2 at 70.degree., concg. the mixt., and treating it with NH4OH to yield a white solid, twice crystd. from PhNO2, then from C6H4Me2, m. 230-2.degree.. The

remainder of the residue was dissolved in 175 ml. CS2 with 2.0 g. AlCl3, the mixt. stirred 1.5 hrs. at room temp., refluxed 15 min., and worked up as usual yielding 0.35 g. unreacted V and only 0.11 g. neutral light brown powder, which yielded no 2,4-dinitrophenylhydrazone.

IT **6926-84-7**, Diphenic acid, methyl ester
(prepn. of)

RN 6926-84-7 CAPLUS

CN [1,1'-Biphenyl]-2,2'-dicarboxylic acid, monomethyl ester (9CI) (CA INDEX NAME)



10082251

CA SUBSCRIBER PRICE -14.97 -14.97

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             0 482359-60-4D
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                 (482359-60-4 (NOTL) 482359-60-4D )

=> s l19
             1 482359-60-4
             0 482359-60-4D
L20          1 482359-60-4/RN
                 (482359-60-4 (NOTL) 482359-60-4D )

=> file caold
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10082251

=> d his

(FILE 'HOME' ENTERED AT 18:31:39 ON 22 JUL 2003)

FILE 'CAPLUS' ENTERED AT 18:31:49 ON 22 JUL 2003

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L1          202 S DIPHENIC (P) (ESTER OR MONOESTER)
L2            3 S L1 AND CHIRAL.
L3            0 S L2 AND BIARYL
L4            0 S L1 AND ACHIRAL
L5            5 S L1 AND CD
L6            4 S L5 NOT L2
L7           57 S DINITRODIPHENIC
L8            7 S L1 AND L7
L9            7 S L8 NOT L2
L10           7 S L8 NOT L6
L11           7 S L10 (P) (ESTER? OR MONOESTER?)
L12           7 S L11 AND ESTER?
L13          18 S L7 (P) (ESTER? OR MONOESTER?)
L14           6 S L13 AND L8
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10082251

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=> s l7 (p) 5
      5451725 5
L15         36 L7 (P) 5

=> s l15 (p) (monoester? or ester?)
        11068 MONOESTER?
       817046 ESTER?
L16         15 L15 (P) (MONOESTER? OR ESTER?)

=> s l16 not l14
L17          9 L16 NOT L14

=> s l17 not l6
L18          9 L17 NOT L6
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10082251

=> d bib abs

L11 ANSWER 1 OF 7 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1961:8131 CAPLUS
DN 55:8131
OREF 55:1625h-i,1626a-f
TI Polycyclic cinnoline derivatives. III. The synthesis of the 4,5,9,10-tetraazapyrene ring system and some nonplanar benzo[c]cinnolines
AU Holt, P. F.; Hughes, A. N.
CS Univ. Reading, UK
SO Journal of the Chemical Society, Abstracts (1960) 3216-21
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA Unavailable
AB cf. CA 54, 4601f. A 4,5,9,10-tetraazapyrene di-N-oxide (I) was prepd. but attempts to prep. 4,5-diazapyrene failed. Several new nonplanar 1,10-disubstituted benzo[c]cinnolines were described. 2-Iodo-3-nitrobenzoic acid (50 g.) refluxed 14 hrs. in 1 l. MeOH satd. with HCl gave 51 g. Me 2-iodo-3-nitrobenzoate (II), m. 62-4.degree.. II (20 g.) treated 25 min. at 160-70.degree. with 17 g. activated Cu bronze, the temp. slowly raised over 15 min. to and kept 0.5 hr. at 210-20.degree., the mixt. cooled, and extd. with C6H6 gave di-Me 6,6'-dinitrobiphenate (III), m. 125-8.degree.. III hydrolyzed to 94% 6,6'-**dinitrodiphenic** acid (IV), m. 255-8.degree.. IV (10 g.) refluxed 3.5 hrs. with 60 ml. SOCl2, the mixt. evapd., and the mixt. added to NH4OH gave 9 g. diamide (V), m. 268-72.degree.. V (10.8 g.) slowly added to a cold soln. of NaOBr (from 4 ml. Br in 13 g. NaOH and 136 ml. H2O), the soln. stirred 10 min., filtered, poured into concd. NH4Cl, and the product crystd. gave 4.26 g. 2,2'-diamino-6,6'-dinitrobiphenyl (VI), m. 242-4.degree. (alc.). VI (0.4 g.) in refluxing 90% alc. treated with 5 g. KOH and 10 g. Zn dust, the soln. refluxed 25 min., filtered, evapd., poured into concd. aq. NaOH, the tar dissolved in alc., the soln. filtered through Al2O3, and the soln. concd. gave 56 mg. unknown substance, m. 86-92.degree.. VI (0.4 g.) in 400 ml. MeOH slowly added to 100 g. 3% Na-Hg, after 4 hrs. the soln. filtered, treated with H2O, and concd. gave 0.21 g. 2,2',6,6'-tetraaminobiphenyl, m. 192-4.degree.. VI (0.5 g.) in 1 l. Et2O refluxed 1 hr. with 2 g. LiAlH4, the mixt. decompd., filtered, the filtrate shaken with 20% HCl, and the acid layer basified gave 160 mg. 1,10-diaminobenzo[c]cinnoline (VII), m. 217-21.degree. (alc.). Satd. aq. Na2S did not affect VI in refluxing alc. VII (160 mg.) in AcOH treated with 15 ml. soln. of 6 ml. 85% H2O2 in 19 ml. AcOH, the soln. heated 1.5 hrs. on the H2O bath, and then evapd. gave 110 mg. 4,5,9,10-tetraazapyrene 4,9(or 10)-dioxide (VIII), decompd. above 270.degree. (HCONMe2). VIII (40 mg.) in 10 ml. concd. HCl treated with the theoretical quantity of SnCl2, the mixt. heated 0.5 hr., poured into excess dil. NaOH, and the ppt. dissolved in alc., and filtered through Al2O3 gave 2.5 mg. red-brown powder, decompd. above 250.degree.. III (2 g.) in 200 ml. dry C6H6 and 500 ml. Et2O treated with 1.25 g. LiAlH4 in 120 ml. Et2O, the mixt. refluxed 20 min., excess LiAlH4 decompd., the mixt. filtered, concd., and the solid in Me2CO filtered through Al2O3 gave 0.18 g. 1,10-bis(hydroxymethyl)benzo[c]cinnoline (IX), m. 227-30.5.degree.. IX with MeI in hot PhNO2 formed the methiodide, m. 160.degree. (decompn.). IX (0.14 g.) in 10 ml. 60% HBr heated 0.5 hr. at 75.degree., the soln. left overnight, poured into dil. NaOH, the ppt. washed, dissolved in Me2CO, and filtered through Al2O3 gave 89 mg. 9,11-dihydro-10-oxa-4,5-diazacyclohepta[d,e]phenanthrene (X), m. 171-2.degree.. If the reaction was carried out 16 hrs. at 200.degree., a black infusible insol. polymer was obtained. X with 80% H2O2 in AcOH gave an N-oxide, m. 224-6.degree.; methiodide m. 185-8.degree.. IX (115 mg.) in 3 ml. SOCl2 refluxed 10 min., the soln. added slowly to dil. KOH, the ppt. washed, and in Me2CO filtered through Al2O3 gave 68 mg. 1-chloromethyl-10-(hydroxymethyl)benzo[c]cinnoline, m. 131-3.degree. (decompn.). When the reaction time was extended to 2 hrs., 57.5% 1,10-bis(chloromethyl)benzo[c]cinnoline (XI) was obtained, m. 171.degree. (decompn.). XI (0.3 g.) in 50 ml. dry PhMe added during 15 min. to 0.4 g. Na in 30 ml. PhMe, the mixt. refluxed 0.5 hr., cooled, filtered, the soln. concd., and filtered through Al2O3 gave only a brown sticky polymeric material.

=> s l11 and ester?
817046 ESTER?
L12 7 L11 AND ESTER?

=> d his

(FILE 'HOME' ENTERED AT 18:31:39 ON 22 JUL 2003)

10082251

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     FILE 'CAPLUS' ENTERED AT 18:31:49 ON 22 JUL 2003
L1          202 S DIPHENIC (P) (ESTER OR MONOESTER)
L2            3 S L1 AND CHIRAL
L3            0 S L2 AND BIARYL
L4            0 S L1 AND ACHIRAL
L5            5 S L1 AND CD
L6            4 S L5 NOT L2
L7           57 S DINITRODIPHENIC
L8            7 S L1 AND L7
L9            7 S L8 NOT L2
L10           7 S L8 NOT L6
L11           7 S L10 (P) (ESTER? OR MONOESTER?)
L12           7 S L11 AND ESTER?

=> s l7 (p) (ester? or monoester?)
        817046 ESTER?
         11068 MONOESTER?
L13         18 L7 (P) (ESTER? OR MONOESTER?)

=> s l13 and l8
L14          6 L13 AND L8

=> d bib abs

L14  ANSWER 1 OF 6  CAPLUS  COPYRIGHT 2003 ACS on STN
AN   1957:56638  CAPLUS
DN   51:56638
OREF 51:10439g-i,10440a-g
TI   Synthesis of mono- and diesters of diphenic and dihydroxydiphenic acids
AU   Patel, Harshadray R.; Blackburn, Dale W.; Jenkins, Glenn L.
CS   Purdue Univ., Lafayette, IN
SO   J. Am. Pharm. Assoc. (1957), 46, 51-5
DT   Journal
LA   Unavailable
AB   Four new dialkylaminoalkyl diphenic monoesters,
     o-HO2CC6H4C6H4CO2R-o (I), were prepd. to study possible neurotropic
     spasmolytic activity by refluxing equimolar amts. of diphenic
     anhydride (0.05 to 0.1 mole) and the amino alc. in 10-50 ml. MeCOEt on a
     steam bath 1-2 hr.  For I, R, recrystg. solvents, % yield, and m.p.
     (uncor.) were given: Et2N(CH2)3, C6H6 and ETOH petr. ether, 56.2,
     139-40.degree.; Bu2N(CH2)3, PrOH, 26.8,109-10.degree.; Me2NCH2CHMe,
     C6H6MeCOEt, 43.9, 133-34.degree.; Et2NCHMeCH2, MeCOEt-aq. Me2CO, 35.9,
     182-83.degree.; Et2N(CH2)3CHMe, EtOH, 20.3, 115-17.degree..  The
     Et2NCH2CHMe ester could not be recrystd.  Four new
     esters, o-EtO2CC6H4C6H4CO2R'.HCl (II), were made from Et H
     diphenate and mono- or dialkylamino alc.  Prepn. A: 0.05 mole of the amino
     alc.-HCl (in 15 ml. CHCl3 and dry HCl) and 0.05 mole Et diphenoyl chloride
     were refluxed.  The 2-isobutylaminoethyl ester was isolated by
     evapg. the CHCl3 and rubbing the HCl salt under Et2O.  The
     1-methyl-2-cyclohexylaminoethyl ester was isolated by adding the
     cooled CHCl3 soln. to 100 ml. 16% Na2CO3, sepg. the CHCl3 layer, extg. the
     aq. layer 4 times with Et2O, drying the combined layers over anhyd.
     Na2SO4, and pptg. as the HCl salt.  Prepn. B: 0.05 mole amino alc. and Et
     diphenoyl chloride were refluxed in 40 ml. C6H6, the solvent evapd., and
     the residue dissolved in 60 ml. H2O, boiled with activated C, and
     filtered.  Addn. of 6N NaOH soln. freed the base to Et2O.  The combined
     Et2O exts. were dried over anhyd. Na2SO4 and the HCl salt pptd. as above.
     The 1-methyl-4-diethylaminobutyl ester resisted all attempts at
     crystn.  Prepn. C: 0.01 mole Et H diphenate was converted to the K salt in
     40 min. by refluxing with KOH pellets in 10 ml. C6H6, 0.01 mole EtI added,
     and the mixt. refluxed 3 hrs., KI filtered off, and C6H6 evapd.  The
     residue was dissolved in dry Et2O and the HCl salt pptd. as above.  For
     II, R, method of prepn., hrs. reflux, recrystg. solvents, % yield, and
     m.p. (cor.) were given: iso-BuNHCH2CH2, A, 12, EtOH, 45.6, 145-46.degree.;
     Et2N(CH2), B, 12, EtOH, 57.6, 109-10.degree.; Me2NCH2CHMe, B and C, 3,
     EtOAc-Et2O and EtOH-petr. ether and EtOH, 28.6, 133.5-4.5.degree.;
     C6H11NHCH2CHMe, A, 120, Et2O, 49.6, 149-50.degree..  Fuming HNO3 (850
     ml.), 80 ml. concd. H2SO4, and 327 g. diphenic acid were mixed
     at 90-95.degree. 6 hrs.  The mixt. was poured on 3 kg. ice and filtered,
     yielding 401 g. pale yellow cryst. mixt. (III) of 4,4' and 4,6'
     dinitrodiphenic acid.  Sn reduction of I in HCl yielded insol. (in
     cold H2O) 4,6'-diaminodiphenic acid-2HCl and the 4,4'-isomer (IV).  Sn was
     pptd. with H2S and IV in soln. was concd. to surface pptn.  The soln. was
     cooled and the pptd. HCl salt was recrystd. from 10-15% HCl, yielding
     56.2% IV; free acid, m. 256-9.degree. (decompn.).  The recrystd.
     4,6'-isomer from 5% HCl soln. yielded the salt whose free acid m.
     327-30.degree. (decompn.)  Diazotization of IV with HNO2 and working up
     gave 4,4'-dihydroxydiphenic acid (V), needles, m. 282-5.degree.
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(decompn.); di-Et ester (VI), m. 151-3.degree. (from 30% EtOH); di-Me ester (VII), m. 209-11.degree.. V (14 g.) refluxed 5 hrs. with 156 g. Ac2O yielded 5.1 g. 4,4'-diacetoxydiphenic anhydride (VIII), m. 216-19.degree. (from PhMe). VIII (5.1 g.) and 55 ml. EtOH refluxed 1-5 hrs. and the excess EtOH evapd. gave 5.5 g. V diacetate mono-Et ester (IX), m. 161.5-63.degree. (from EtOH), neutral equiv. 398. V (10 g.) dissolved in 100 ml. 10% NaOH, 15.8 g. Me2SO4 added in two portions with agitation 1 hr., refluxed 2 hrs., 4 g. NaOH in 5 ml. hot H2O added and the soln. refluxed 2 hrs. and acidified with 15 ml. concd. HCl gave 9.57 g. di-Me ether (X), m. 241-3.5.degree., neutral equiv. 150. X anhydride (7 g.) refluxed 1 hr. with 35 ml. abs. EtOH gave 5.2 g. V di-Me ether mono-Et ester (XI), m. 139-142.degree., neutral equiv. 293. XI (5.2 g.) in 40 ml. dry C6H6 was refluxed 7 hrs. with 4.0 g. SOCl2 and the mixt. subjected to vacuum distn., C6H6 twice added and evapd. The residual oil failed to evap. at 0.4 mm. Recrystn. of the acid chloride from petr. ether-C6H6 gave orange crystals, m. 119-21.degree.. The acid chloride with 1.87 g. 2-diethylaminoethanol in 50 ml. C6H6 was refluxed 2.5 hrs. The HCl basic ester was sepd. by extn. with very dil. HCl. Addn. of 10% Na2CO3 to the exts. freed the XI 2-diethylaminoethyl ester, which was extd. with Et2O, dried, and the Et2O evapd. The oil was heated at 100.degree. (in vacuo) removing the slight excess of amino alc., redissolved in cold Et2O, and the HCl salt pptd. by dropwise addn. of a satd. soln. of dry HCl in anhyd. Et2O. The same procedure applied to the prepn. of 2-diethylaminoethyl 2-carbethoxy-4,4'-dihydroxy-2'-biphenylcarboxylate, using IX, failed. Hydrolyzing the Ac groups of the HCl salt with 5% Ba(OH)2 split off the ester groups, giving V.

=> d 2-6 bib abs

L14 ANSWER 2 OF 6 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1955:77755 CAPLUS
DN 49:77755
OREF 49:14685a-d
TI Synthesis of 4-amino- and 4-amino-4'-nitrodiphenic acids methyl esters
AU Tsukerman, S. V.; Litvinenko, L. M.; Grekov, A. P.
CS A. M. Gor'ki State Univ., Kharkov
SO Ukrains'kii Khemichnii Zhurnal (1955), 21, 341-3
CODEN: UKHZAS; ISSN: 0372-4190
DT Journal
LA Russian
AB Adding concd. NH3 to 6 g. 4,4'-dinitrodiphenic acid (I) in 180 ml. MeOH to Congo red, refluxing, adding dropwise under agitation 60 ml. N Na disulfide in MeOH-H2O (1:1), boiling 45 min., adding concd. HCl until blue appears, evapg. on the steam bath, extg. several times with boiling 1:1 HCl-H2O, and cooling, gave 4.6 g. (75%) 4-amino-4'-nitrodiphenic acid hydrochloride (II), pale yellow crystals, decomp. above 350.degree.. II dissolved in H2O, 2% NH4OH added dropwise, the ppt. filtered, washed, and dried in vacuo at 100.degree., gave 4-amino-4'-nitrodiphenic acid (III), yellow crystals, m. 249-50.degree., sol. in pyridine, acidic or basic aq. solns., slightly sol. in EtOH, glacial AcOH, and H2O, insol. in Et2O and MeCHCl2. Refluxing 4 g. III 6 hrs. in 80 ml. abs. MeOH satd. with dry HCl, cooling, the mixt. poured into 5% NH4OH, the ppt. filtered, water-washed, dried in vacuo at 100.degree., gave 74% Me ester, yellow crystals, m. 165-6.degree. (from MeOH), sol. in EtOH, Et2O, and hot H2O, difficultly sol. in cold H2O. Similarly was prepd. the 4-aminodiphenic acid methyl ester (72%), colorless crystals, m. 101-2.degree. (from MeOH-H2O), sol. in EtOH, Et2O and hot H2O. The Me ester of m-H2NC6H4CO2H, carefully prepd. by a similar process, m. 53-4.degree..

L14 ANSWER 3 OF 6 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1955:39430 CAPLUS
DN 49:39430
OREF 49:7552d-i,7553a-d
TI Photochemical reactions. IV. The photosynthesis of cyclic sulfuric acid esters by the addition of SO2 to o-quinones
AU Schenck, Gunther O.; Schmidt-Thomee, Georg A.
CS Univ. Gottingen, Germany
SO Ann. (1953), 584, 199-220
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB To confirm the conclusions that the photosensitizer forms an intermediate with the double role of dehydrogenating another mol. and adding mol. O, a phototropic diradical is sought whose free valence on O could be dehydrogenating, and on C add O. This must be preceded by the study of a

diradical with 2 free O valences, then of one with 2 free C valences. 9,10-Phenanthrenequinone (I) should yield such a radical and react with SO2 as does a Cl atom (cf. Bonhoeffer, C.A. 17, 2392). A diagram of the app. shows the closed reaction vessel into which dips another closed, double-walled, H2O-cooled tube contg. the Hg vapor lamp. The soln. or suspension of o-quinone in C6H6 is satd. with SO2 before introduction into the reaction vessel. The photoreaction (no reaction in the dark) is formulated below. The hitherto unknown cyclic sulfuric acid **esters**, confirm the existence of intermediate phototropic diradicals. All these cyclosulfates are decompd. by heat to SO2 and the parent quinones. Wt. o-quinone, hrs. of illumination, wt. cyclosulfate formed, m.p., are : 25 g. I, 80, 28-30 g. (86-92%), 202-3.degree. (decompn.); 5 g. 3-nitro deriv. (II) of I, 53, 1.1 g. (17.5%), 190-1.degree. (decompn.); 5 g. 2-nitro deriv. (III) of I (cf. Schmidt and Spoun, C.A. 16, 3650), 60, 3 g. (48%), 204-6.degree. (decompn.); 1 g. 4-nitro deriv. (IV) of I, 20-5, 0.5 g. (40%), 185-6.degree. (decompn.); 30 g. tetrachloro-o-benzoquinone (V), 40, 25 g. (57%), 125-6.degree.; 12 g. o-naphthoquinone (VI), 200, 5.5 g. (33%), 73-4.degree.; 2 g. 3-nitro deriv. of VI, 20, 1.2-1.7 g. (45-65%), 143.degree.; 12 g. chrysoquinone (VII), 90-100, 12 g. (81%), 221-2.degree. (decompn.). The only previously reported compd. contg. C:C in a cyclosulfate ring is the intermediate product (VIII) in the prepn. of alizarinbordeaux (IX) from alizarin (X) with 75% oleum [cf. Schmidt, J. Prakt. Chem. 43, 239(1891)]. This prepn. was repeated to yield 1.6 g. (87%) VIII from 1.5 g. X, and its absorption max. (567 m.mu.) differed markedly from those of X (496 and 549 m.mu.) and IX (531 and 577 m.mu.), and from the hydrolysis and thermal decompn. products of VIII (same as IX). Analogous results from the cyclosulfate (XI) of II helped prove the course of the reaction for all cyclosulfates. Alk. hydrolysis of 3 g. XI gave 2.5-2.7 g. (59-63%) di-Na salt of the sulfuric acid half **ester**, (XII), with indicator properties, and acid hydrolysis of XII gave 3-nitro-9,10-dihydroxyphenanthrene, m. and mixed m.p. 221-3.degree. [cf. Schmidt and Kampf, Ber. 35, 3125(1902)]; Ac, deriv., m. and mixed m.p. 239-40.degree. (decompn.). Reduction of XI with Fe and glacial AcOH gave the corresponding unstable amino compd., m. 175-7.degree. (decompn.); Ac deriv., m. 198-213.degree. (decompn.). The cyclosulfate (XIII) of I and that of VI were stable toward both acid and alk. hydrolysis. Nitration of XIII resulted in XI (proved by thermal decompn. to the known II), or the 3,6-dinitro deriv. (XIV) of XIII, 55-60% yield, m. 240-1.degree. (decompn.). Thermal decompn. of XIV yielded SO2 and the 3,6-dinitro deriv. (XV) of I (73%), m. 293-6.degree. (from Ac2O) (decompn.); monoxime, m. 209-10.degree. (from glacial AcOH) (decompn.); quinoxaline (from o-phenylenediamine), m. 359-62.degree. (from C5H5N) (decompn.). XV was identified by bichromate oxidation to 5,5'-**dinitrodiphenic** acid, m. 286-8.degree.; Me **ester**, m. 160-1.degree.. Reduction of the cyclosulfate of IV gave a compd. whose analysis agreed with the corresponding amino compd. with 1 mol. Me2CO, m. 172-3.degree. (from Me2CO-MeOH). The cyclosulfate of V reacted with PhNH2 to give a colorless, unidentified, S-free, N-contg. compd., m. 90-4.degree. (decompn.) (from CCl4). Reduction of the cyclosulfate of VI gave the corresponding amino deriv., m. 139-41.degree. (decompn.) (from dil. MeOH). Attempts to apply similar cyclosulfate synthesis to .alpha.-diketones and to p-quinones were unsuccessful. The evidence here given for the independent existence and exclusively photochemical formation of the phototropic diradicals with typical O-radical quality gives an exptl. soln. for the old problem of the valence tautomerism of quinones.

L14 ANSWER 4 OF 6 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1930:12349 CAPLUS
DN 24:12349
OREF 24:1367d-h
TI Biphenyl. 5,5'-Substituted diphenic acids
AU Pufahl, Fritz
SO Ber. (1929), 62B, 2817-24
DT Journal
LA Unavailable
AB The theory of Mills and Meisenheimer that the optical activity of certain derivs. of Ph2 is due to a mech. hindrance of the free rotation of the C6H6 nuclei by substituents adjacent to the point of union of the nuclei is supported by the fact that the 6- and 6,6'-substituted derivs. of **diphenic** acid (I) are resolvable into optical isomers while the 4,4'-derivs. are not. The theory is further confirmed by the present work, in which it was found impossible to resolve 5,5'-derivs. into optical isomers; furthermore, these 5,5-derivs., like the 4,4'-compds. and I itself, can be readily converted into their anhydrides. 2,4-I(O2N)C6H3CO2H, m. 146-7.degree. (all m. ps. are cor.), was obtained in 19-g. yield from diazotized com. 2,4-H2N(O2N)C6H3CO2H (18 g.) and KI; its Me **ester**, m. 94.degree., with reduced Cu at 200.degree. gave

75% of the yellow di-Me **ester**, m. 161.degree., of 5,5'-**dinitrodiphenic** acid (II), yellow, m. 285-7.degree. (decompn.), seps. from MeOH in light yellow needles with 2 mols. solvent, converted by boiling Ac2O into the anhydride; m. 265.degree., insol. in cold dil. Na2CO3. Brucine salt, C60H60O1N6, m. 190-200.degree., sol. in 100 parts hot water; all fractions obtained by crystn. from H2O showed the same m. p. and gave an optically inactive II. 5,5'-Diantinodiphenic acid (III), from II with Na2S in boiling dil. Na2CO3 or from 2,4-H2N(AcNH)C3H3CO2H (m. 215.degree. (decompn.), and not 193-4.degree. as given in Ger. pat. 212,434) converted into the N,N'-di-Ac deriv. of III by diazotization and treatment with NH4OH-CuSO4 and hydrolyzed to III with hot NaOH, m. 265.degree. (decompn.); di-Me **ester**, m. 220-2.degree.. N,N'-Di-Ac deriv., becomes yellow above 300.degree., then darkens and shows no distinct m. p. up to 430.degree.. N,N'-Di-Bz deriv., m. 340-1.degree. (decompn.), forms a brucine salt, m. 198-200.degree., [.alpha.]D20-26.90.degree. (CHCl3, 1.75% soln.), from which no active acid could be recovered; anhydride, m. 283-4.degree. (decompn.) (a sample prepd. with (EtCO)2O instead of Ac2O m. 288-9.degree. (decompn.)); mono-Et **ester**, from the anhydride and boiling EtOH, m. 174.degree., easily col. in cold dil. Na2CO3; manolide m 291-2.degree. (decompn.), very easily sol. in dil.Na2Co3. N,N'-Di-p-nitrobenzoyl deriv., m. 350-2.degree.; m-isomer, m. 274.degree., yields an anhydride, m. 296-7.degree.

L14 ANSWER 5 OF 6 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1924:23404 CAPLUS
DN 18:23404
OREF 18:3186a-d
TI Diphenic acid series. II
AU Underwood, H. W., Jr.; Kochmann, E. L.
SO Journal of the American Chemical Society (1924), 46, 2069-78
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
AB cf. C. A. 18, 1832. In the oxidation of phenanthrene the max. yield of the quinone (45%) was obtained when a 350% excess of the Na2Cr2O7 was used (1.53 g. 96% H2SO4 and 2.5 g. H2O were used for each g. of Na2Cr2O7). An equiv. amt. of K2Cr2O7, gave a 56% yield. Further oxidation to **diphenic** acid gave the following yields: Five g. glacial AcOH for 1 g. quinone and 750% excess K2Cr2O7, 70% yield. Substitution of 56% AcOH increased this to 74%. Na2Cr2O7 (750% excess) and glacial AcOH gave a 76% yield. Phenoldiphenein does not give an oxime under conditions employed for the production of such a deriv. of phenolphthalein. When **diphenic** acid dichloride, diamide, di-Et **ester**, di-Me **ester**, Et **ester**, Me **ester**, monoamide and imide are heated with concd. H2SO4, each compd. is transformed into a member of the diphenyleneketone-4-carboxylic acid series, the yields being given in a table. These changes involve rotation of the rings in the Ph2 nucleus. The mechanism of the reaction has not been precisely detd., since hydrolysis occurs in every case, even when special precautions are taken. No isomerization of phenanthridone was brought about by treatment with H2SO4. p,p'-**Dinitrodiphenic** acid is unique in that it does not form an anhydride or a ketone acid; a plausible explanation of the behavior of this compd. may be found in postulating that the m-orienting NO2 group in each ring loosens the HO group in the CO2H and strengthens the bond which holds the H atom in the latter as well as the force holding the ring H which is m to the NO2 group. The action of heat or of fuming SnCl2 does not isomerize phenoldiphenein. If the latter be maintained for some time at a temp. slightly above its m. p., CO2 is evolved.

L14 ANSWER 6 OF 6 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1921:13055 CAPLUS
DN 15:13055
OREF 15:2434b-i
TI A second form of 6,6'-**dinitrodiphenic** acid and its conversion into new cyclic systems
AU Kenner, James; Stubbings, Wilfrid V.
CS Univ. Sheffield
SO Journal of the Chemical Society, Abstracts (1921), 119, 593-602
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA Unavailable
GI For diagram(s), see printed CA Issue.
AB 6,6'-**Dinitrodiphenic** acid was first prepared by Schulze (Ann. 203, 95) who found the m. p. to be 297.degree.; this was obtained by nitrating **diphenic** acid and also by oxidizing the di-NO2 deriv. of phenanthraquinone. The synthetic acid, from (CO2H)NO2C6H3I, m. 263.degree., and is called the .gamma.-acid, since Schulze termed his

product the .beta.-acid. Chem. reactions indicate that this is really a new form and that the two are probably stereoisomeric:Methyl 2-Chloro-3-nitrobenzoate, C8H6O4NCl, needles, m. 70.degree.. Ethyl ester, C9H8O4NCl, b. 314.degree.. The Me ester, treated at 210.degree. with Cu powder and then heated 1 hr. at 225-235.degree., gave methyl .gamma.-6,6'-dinitrodiphenate, C16H12O8N2, pale yellow, hexagonal plates, m.132-3.degree.. Ethyl ester, prepd. from ethyl 2-iodo-3-nitrobenzoate (large, tabular crystals, m. 54.degree. large yellow crystals, m. 140-2.degree.. Sapond. with H2SO4, .gamma.-6,6'-dinitrodiphenic acid was obtained, thin plates, m. 263.degree.. The stannous, silver, lead, ferric and copper salts are sparingly sol. in hot H2O; the mercuric, cobalt, calcium, magnesium and barium salts are sol. in H2O. The acid does not yield an anhydride when heated with Ac2O. Chloride, prisms, m. 157.degree.. Amide, C14H10O6N4, m. 276.degree.. Dianilide, C25H18O6N4, flat, diamond-shaped crystals, m. 232-4.degree. (decompn.). The hydrazide, C14H8O6N4, by shaking the chloride with N2H4.H2O, did not m. 290.degree.. Diacetate of the hydrazide, C18H12O8N4, small prisms, m. 214-5.degree.. It would appear that a change of configuration occurs in this reaction, and that upon hydrolysis of the .gamma.-acid chloride the .beta.-acid might be obtained; expt. showed that the original acid was recovered. 6,6'-Diamino-z,z'-ditolyl, C14H16N2, clusters of slender needles, m. 136.degree.. Diacetate, clusters of transparent needles, m. 205.degree.. Upon oxidation with KMnO4 and Mg2SO4 in H2O, .gamma.-6,6'-diacetylaminodiphenyl acid was obtained as large prismatic needles, did not m. 300.degree.. This indicates that inversion occurs either during reduction or during the conversion into the acid. Upon reduction of the .gamma.-acid, the dilactam of .gamma.-6,6'-diaminodiphenic acid (I) is formed, pale yellow needles; it was also obtained from the di-Ac deriv. by heating with Ac2O for 10 hrs., or by boiling with 70% H2SO4 for 25 min. The soln. in concd. H2SO4 has blue fluorescence. The reduction of 6,6'-dinitroditolyl with Na-Hg gave 1,10-dimethyl-5,6-naphthaisodiazine (II), yellow, transparent prisms, m. 96-7.degree..

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L18 ANSWER 1 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2001:615131 CAPLUS
DN 136:5585
TI Chirality transmission in flexible 5,5'-**dinitrodiphenic esters** connected with chiral secondary alcohols
AU Hosoi, S.; Kamiya, M.; Kiuchi, F.; Ohta, T.
CS Faculty of Pharmaceutical Sciences, Kanazawa University, Kanazawa, 920-0934, Japan
SO Tetrahedron Letters (2001), 42(36), 6315-6317
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier Science Ltd.
DT Journal
LA English
AB Induced CD (CD) was obsd. with dinitrodiphenic esters of chiral secondary alcs. The CD spectra of the esters prepd. from a pair of antipodal alcs. were sym. to each other relative to the x-axis, indicating the enantiomeric nature of the esters. The sign of the Cotton effect at around 270 nm was found to reflect the abs. configuration of the original alc. In the case of aliph. mono-alcs., neg. Cotton effect was obsd. for the esters of (R)-alcs. and a pos. effect for the esters of (S)-alcs. On the contrary, unsatn. or an oxygen atom at the vicinal position reversed the sign of the Cotton effect.
RE.CNT 8 THERE ARE 8 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d 2-9 bib abs

L18 ANSWER 2 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2001:101974 CAPLUS
DN 134:375498
TI A method for determination of absolute configuration of chiral alcohol using achiral biaryl chromophore
AU Hosoi, Shinzo; Kamiya, Makiko; Ohta, Tomihisa
CS Faculty of Pharmaceutical Sciences, Kanazawa University, Japan
SO Tennen Yuki Kagobutsu Toronkai Koen Yoshishu (2000), 42nd, 571-576
CODEN: TYKYDS
PB Nippon Kagakkai
DT Journal
LA Japanese
AB Since the exciton-coupled CD was extensively applied to various org. compds. to det. their abs. configurations in a nonempirical manner, the CD spectroscopic anal. was regarded as a reliable tool as x-ray diffraction method for stereochem. elucidation. However, application of this method was limited to chiral compds. with two or more functional groups. Recently, Harada and coworkers disclosed a novel CD strategy for detg. an abs. configuration of chiral mono-alc. The authors report here a new method to det. abs. configuration of chiral alcs. using achiral diphenic acid derivs. as CD auxiliary. Thus, 5,5'-**dinitrodiphenic** anhydride was condensed with L-, D-menthol to give Me **esters** after methylation. Their CD spectra did not exhibit an exciton split CD Cotton effect unexpectedly but showed sym. CD curves on an x axis. This indicates that chirality of alcs. was effectively transmitted to a biphenyl chromophore. Solvent and substituent effects were studied further. Other chiral alcs. were similarly derivatized with 5,5'-**dinitrodiphenic** anhydride. Their CD spectra showed a definite tendency. Alcs. employed are classified into two groups by structural feature (A: unsatd. type; B: satd. type). In group A Cotton effect of (R)-alcs. around 270 nm was pos., whereas that of (S)-alcs. was neg. However, opposite phenomenon was recognized in group B. Practical usefulness of the present method is demonstrated by the detn. of abs. configuration of dihydroxybergammotin isolated from grapefruit juice. The difference CD spectrum of and its 5,5'-**dinitrodiphenic** anhydride deriv. exhibited a neg. Cotton effect around 270-280 nm. The configuration was thus assigned to be R.

L18 ANSWER 3 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1965:44090 CAPLUS
DN 62:44090
OREF 62:7816c-h,7817a-h
TI Stereochemistry of pinidine
AU Hill, R. K.; Chan, T. H.; Jo le, J. A.
CS Princeton Univ., Princeton, NJ
SO Tetrahedron (1965), 21(1), 147-61

10082251

CODEN: TETRAB; ISSN: 0040-4020
DT Journal
LA English
GI For diagram(s), see printed CA Issue.
AB cf. CA 57, 7219e. Pinidine (I) (1.2 g.), from Pinus sabiniana, in 20 ml. Et2O refluxed 30 min. with EtMgBr (1.22 g. EtBr, 0.27 g. Mg) in 20 ml. Et2O, the mixt. refluxed 1 hr. after addn. of 1.2 g. BzCl in 10 ml. Et2O, the cooled soln. dild. with H2O, the washed (dil. HCl, dil. NaOH) and dried Et2O evapd., and the residue chromatographed over Al2O3 and eluted with C6H6 gave 1.5 g. oily amide (II), also prepd. from I and BzCl in C5H5N. II (2.6 g.) in 100 ml. 4:1 Me2CO-H2O treated portionwise with 6.4 g. KMnO4, the mixt. stirred 1 hr. at 50.degree. and 16 hrs. at 20.degree., the filtered soln. concd. and partitioned between Et2O and H2O, the aq. layer acidified and extd. with Et2O, the oily acid (1.8 g.) adsorbed on Al2O3, the column washed with CHCl3, the acid eluted with aq. NaHCO3, and the acidified eluate extd. with Et2O gave (+)-N-benzoyl-6-methylpipecolic acid [(+)-III], m. 128-9.degree. (CCl4, petr. ether), [.alpha.]20D 207.degree. (c 0.01, CHCl3). C6H6-EtOH (175 ml. 3:2 mixt.) contg. 10 g. 6-methylpicolinic acid refluxed 30 min. over 20 g. MgSO4 in a Soxhlet thimble in a stream of dry HCl, the mixt. refluxed 18 hrs., the residue on evapn., partitioned between C6H6 and 20% aq. NaOH, and the dried C6H6 layer distd. gave 7.5 g. Et 6-methylpicolinate, b18 133.degree.; amide m. 114-16.degree.. The ester (5 g.) in 75 ml. alc. and 2 ml. concd. aq. HCl hydrogenated over 0.15 g. prereduced PtO at 20.degree./3 atm. and the hot filtrate cooled gave cryst. Et 6-methylpipecolate-HCl, m. 237-8.degree.. The salt (19.75 g.) and 15.4 g. BzCl in 100 ml. C5H5N stirred 4 days yielded Et N-benzoyl-6-methylpipecolate, m. 69.5-70.5.degree., hydrolyzed by refluxing 0.85 g. in 20 ml. 10% aq. NaOH 4 hrs. and acidified to give 0.55 g. acid, m. 140-1.degree., and recrystd. from CHCl3-CCl4 to give racemic III, m. 141.5-2.5.degree.. Strychnine (6.69 g.) and 4.94 g. dl-III taken up in 50 ml. boiling 4:1 EtOH-H2O, the cooled soln. dild. with 200 ml. EtO and kept 24 hrs., and the ppt. (5.4 g.) recrystd. from CCl4-petr. ether gave 2.0 g. salt, m. 148-9.degree., [.alpha.]20D -51.7.degree.. The salt (1.5 g.) in H2O made alk. to liberate 0.82 g. strychnine and the aq. soln. acidified yielded 0.25 g. l-III, recrystd. from CHCl3-petr. ether to give a sample, m. 122-3.degree., [.alpha.]20D -180.degree. (CHCl3). The filtrate from the original sepn. evapd., the residue taken up in hot alc., the acid regenerated, and the material (2.5 g., [.alpha.]20D 119.degree.), recrystd. 4 times from CHCl3-petr. ether gave (+)-III, m. 128-9.degree., [.alpha.]20D 185.degree.. LiAlH4 (0.76 g.) in 20 ml. tetrahydrofuran (THF) refluxed with dropwise addn. of 2.47 g. (+)-III in 20 ml. THF and the mixt. refluxed 18 hrs. yielded 2.2 g. N-benzyl-2-hydroxy-methyl-6-methylpiperidine (IV), [.alpha.]20D -21.7.degree. (c 0.025, CHCl3); picrate m. 119-20.degree. (alc.-Et2O). Racemic III similarly gave racemic IV; picrate m. 121-2.degree.. The alc. (-)-IV (2.0 g.) added cautiously to 35 ml. ice-cold SOCl2, the mixt. refluxed 3 hrs., excess SOCl2 evapd., and the residue poured onto crushed ice, made alk. with cold 20% aq. NaOH, and extd. with Et2O gave 1.4 g. oily N-benzyl-2-chloromethyl-6-methylpiperidine (V), [.alpha.]20D -3.2.degree. (CHCl3). The similarly prepd. racemic V gave a picrate, m. 95-7.degree. (alc.-petr. ether). V (1.4 g.) and 1.3 g. LiAlH4 refluxed 16 hrs. in 100 ml. THF and the product (1.2 g. oily base) examd. by vapor phase chromatography showed the presence of 3:4 N-benzyl-2-cis-2,6-dimethylpiperidine (VI)-N-benzyl-2-methylazacycloheptane (VII). The isomeric N-benzyltraus-2,6-dimethylpiperidine had retention time 4.60 min. Identification of the products was made by independent synthesis. Na (250 g.) added portionwise to 107 g. 2,6-lutidine in 2 l. alc., the cooled soln. dild. with 1 l. H2O, the alc. evapd., the soln. dild. with 1 l. H2O and steam-distd., the acidified distillate concd., made alk., and extd. with Et2O, the dried ext. distd., and the mixed bases (55 g., b. 127-35.degree.) sepd. by 3 fractionations through an 18-in. spinning band column gave 26.5% cis-2,6-dimethylpiperidine (VIII), b. 126-7.degree. (HCl salt m. 289-91.degree.), and 8.9% trans-2,6-dimethylpiperidine (IX), b. 136-7.degree.; HCl salt m. 289-91.degree.; N-Bz deriv. (X), m. 54-5.degree.. VIII (1.1 g.) and 2.32 g. D-camphor-10-sulfonic acid boiled in 5 ml. alc. and the cooled soln. dild. with 10 ml. Et2O and 8 ml. petr. ether yielded 1.8 g. D-camphor sulfonate, m. 159-60.degree., regenerated to give optically inactive VIII, similarly recovered from VIII D-camphorate, m. 186-8.degree.(alc.). VIII was converted to the N-Bz deriv. (XI) m. 110.degree.. LiAlH4 redn. of X and XI gave quant. yields of VI; HCl salt m. 177-9.degree.; reineckate m. 158-60.degree.. IX (1.1 g.) treated with 1.66 g. (-)-dinitrodiphenic acid ([.alpha.]20D -120.degree.) in 10 ml. alc., the salt (2.59 g., m. 269-72.degree.) recrystd. from alc., and the 1st crop (0.46 g., m. 271-6.degree.) acidified with HCl and washed with Et2O gave 0.125 g. (+)-IX, [.alpha.]20D 2.8.degree. (v 4.0, alc.).

Schmidt rearrangement of 2-methylcyclohexanone (Blicke and Doorenbos, CA 49, 8312f) and LiAlH4 redn. of the lactam gave 2-methylazacycloheptane, converted to the HCl salt, m. 198-200.degree., stirred 18 hrs. with an equal wt. of BzCl in 10% aq. NaOH, and extd. with Et2O and the amide (1.45 g.) refluxed 16 hrs. with 0.25 g. LiAlH4 in 45 ml. Et2O gave 1.0 g. VII; reineckate 158.degree. (decompn.) (60% alc.). The lack of optical activity of VI established the relative stereochemistry at the 2- and 6-position of I as cis. The formation of VII undoubtedly involved the intermediate ethylene immonium ion formed by neighboring group participation of the N atom. An alternative route of degradation of III to circumvent this rearrangement was sought. LiAlH4 (0.42 g.) in 20 ml. Et2O added dropwise to 5.5 g. Et N-benzoyl-6-methylpipecolate in 40 ml. Et2O at -20.degree. and stirred 1 hr. before decompn. with a small amt. of H2O, the dried filtrate concd., and the residue (2.25 g., m. 98.degree.) recrystd. from CHCl3-petr. ether yielded the alc. (XIII, R = OH) (XIV), m. 99.degree.; XIV (0.35 g.) in 10 ml. C6H6 refluxed 1 hr. with 0.30 ml. SOCl2, the washed (H2O, 10% aq. NaOH, H2O) and dried soln. concd., the oil (0.38 g.) refluxed 25 min. in 15 ml. 95% alc. contg. 0.40 g. SC(NH2)2 and 0.40 g. KI, the soln. (12 ml.) shaken 30 min. with Raney Ni, the filtered soln. evapd., the oil taken up in Et2O, satd. with gaseous HCl, and the ppt. recrystd. from EtOH-Et2O-petr. ether gave 2-benzoyloxymethyl-6-methylpiperidine (XV); HCl salt m. 248.degree.; N-Bz deriv. identical with XIV benzoate. XIV (0.10 g.) in 3 ml. hot 2N HCl cooled and filtered gave quant. XV HCl salt. XIV (0.58 g.) in 15 ml. C6H6 refluxed 1.5 hrs. with 0.5 ml. SOCl2 and 1.5 ml. C5H5N, the cooled, H2O-washed and dried soln. concd., the oily chloride XIII (R = Cl) (0.52 g.) in 10 ml. C6H6 added dropwise to a hot stirred mixt. of 0.62 g. PhCH2SH and 0.20 g. powd. KOH in 15 ml. C6H6, the mixt. refluxed 1.5 hrs., the oily product (0.58 g.) shaken 1.5 hrs. in 15 ml. alc. with 1 g. Raney Ni, the residue on evapn. of the filtered soln. partitioned between Et2O and 2N HCl, the acid soln. concd. to give 0.10 g. XV.HCl salt, the Et2O soln. evapd., and the residue chromatographed on Al2O3 and eluted with CHCl3 gave N-benzoyl-cis-2,6-dimethylpiperidine, m. 99-100.degree., identical with synthetic XI. The stereochemistry of the double bond in I was established as trans by both ir and N.M.R. spectrometry. The abs. configuration was elucidated by eliminating one of the asym. centers of I and relating the other to a substance of known configuration. I (0.73 g.) in 10 ml. MeI refluxed 3 hrs. with 10 ml. 10% aq. K2CO3 with stirring, the MeI distd., and the cooled soln. washed with Et2O and extd. with CHCl3 yielded 1.7 g. hygroscopic cryst. N-methylpinidine-MeI, m. 109-10.degree., hydrogenated over prereduced PtO2, the filtered soln. acidified, the residue on evapn. partitioned between Et2O and H2O, and the aq. layer made alk. with K2CO3 and extd. with Et2O to yield (+)-N,N-dimethyl-2-nonylamine [(+)-XVI], b. 177-9.degree., [.alpha.]20D 7.04.degree. (CHCl3); MeI salt m. 245-7.degree. (EtOAc), [.alpha.]20D 12.25.degree. (CHCl3). Treatment of (+)-2-nonanol [85% optically pure, [.alpha.]20D 7.68.degree. (CHCl3)] with PBr3 and distn. at 120-5.degree./20 mm. gave (-)-2-bromononane (1.4 g., [.alpha.]20D -25.20.degree., CHCl3), which with 0.32 g. Et2NH heated 24 hrs. in 2 ml. C6H6 in a sealed tube at 110.degree., the cooled product partitioned between Et2O and dil. HCl, and the aq. layer made alk. with K2CO3 and extd. with Et2O yielded 0.40 g. (-)-XVI, b. 173-5.degree., [.alpha.]20D -7.15.degree. (CHCl3); MeI salt m. 245-7.degree., [.alpha.]20D -16.91.degree. (CHCl3), ir spectrum identical with that of (+)-XVI MeI salt. Accordingly the stereochemistry of I was established as 2-(R)-methyl-6-(R)-(2-trans-propenyl)piperidine.

L18 ANSWER 4 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1961:45588 CAPLUS
DN 55:45588
OREF 55:8821c-f
TI Composition of a Lurgi brown coal tar. III. Neutral oil fractions boiling from 30 to 130.degree. and 130 to 172.degree.
AU Brown, I.
CS Div. Phys. Chem., C.S.I.R.O., Melbourne
SO Australian Journal of Applied Science (1960), 11, 403-33
CODEN: AJACA3; ISSN: 0572-1156
DT Journal
LA Unavailable
AB cf. CA 53, 22839e. Neutral oil fractions b. 30-130.degree. (A, 13.03% of tar) and b. 130-172.degree. (B, 12.69% of tar), sepd. as described by Brown (CA 53, 22839e) were fractionated by displacement chromatography on silica gel into paraffins (5% of A, 7% of B), olefins (10% of A, 15% of B), aromatics (78% of A, 67% of B), and nonhydrocarbons (7% of A, 11% of B); these fractions were further subdivided, if necessary, by distn., and components were then identified by relative retention times when submitted to vapor-phase chromatography on 3 different stationary phases. Major components are (with fraction in which they occur and wt. %

of fraction): n-C6H14, A 0.2; n-C7H16, A 0.9; n-C8H18, A 2.0, B 0.1; n-C9H20, A 0.5, B 2.1; n-C10H22, B 2.8; n-C11H24, B 0.5 ; 1-hexene, A 0.9; 1-heptene, A 1.8; 1-octene, A2.6, B 0.1; 1-nonene, A 0.7, B 3.8; 1-decene, B 5.9; 1-undecene, B 0.9; benzene, A 24.0; toluene, A 44.0, B 0.2; PhEt, A 2.9, B 5.2; m-xylene, A 4.3, B 13.0; p-xylene, A 1.5, B 4.7; o-xylene. A 1.2, B 8.1; m-C6H4MeEt, B 5.0; p-C6H4MeEt, B 2.9; o-C6H4MeEt, B 2.8; 1,3, 5-C6H3Me3, B 1.8; 1,2,4-C6H3Me3, B 5.9; 1 2,3-C6H3Me3, B 3.2; indan, B 2.3; indene, B 2.7; styrene, B 1.7; MeCOEt, A 1.1; MeCOPr, A 1.7; MeCOBu, A 0.7, B 0.1; Me(CH2)4COMe, B 0.8; Me(CH2)5COMe, B 0.6; coumarone, B 5.6. Relative retention times on Apiezon L, benzylbiphenyl and the di-n-octyl **ester** of 4,4'-**dinitrodiphenic** acid, at 100.degree. (some also at 75.degree. and 150.degree.), are given for oil constituents and nearly 200 reference compds. In all, 144 compds. were shown to be present in the oils, including some furans and thiophenes.

L18 ANSWER 5 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1955:56586 CAPLUS
DN 49:56586
OREF 49:10886d-g
TI Tuberculostatic activity of some derivatives of p-aminobenzoic acid
AU van der Stelt, C.; Voorspuij, A. J. Zwart; Nauta, W. Th.
CS Amsterdam Univ. Hosp.
SO Antonie van Leeuwenhoek (1954), 20, 285-98
CODEN: ALJMAO; ISSN: 0003-6072
DT Journal
LA Unavailable
AB The following compds. were tested: 4-nitrobenzoic acid (I) and its Me, Et, Pr, iso-Pr, cyclopentyl, 1,3-di-methylbutyl, 2-ethylbutyl, 1-methylhexyl, 2-ethylhexyl, 2,6-dimethyl-4-heptyl, 3,5,5 -trimethylhexyl, and 3,5,5-trimethylcyclohexyl **esters**, I hydrazide, 3-methyl-4-nitrobenzoic acid, 4-nitroisophthalic acid, 4-nitrophenylacetic acid (II) and its Me and Et **esters**, 5-nitro-2-furoate, Me 5 -nitro-2-thiophenecarboxylate, Me 4-amino-3,5-dichlorobenzoate, 3,3'-diamino-5,5'-dicarboxydiphenyl, the Me and Pr **esters** and the hydrazide of 4-H2NC6H4CO2H (IIa), (4-H2NC6H4CO)2, (4-AcNHC6H4CO)2, 4,4'-diacetylaminobenzoin, (4-H2NC6H4)2CO, (4-AcNHC6H4)2CO, (4-H2NC6H4)2CH2, 4-AcNHC6H4CHO, "4-(benzoyl-thioureido)benzoic acid," 4-aminophenylacetic acid (IIb), Et **ester** of IIb, hexahydrobenzoic acid lactam (sic), 2-amino-5 -carboxypyridine, Et 5-amino-2-furoate, Et 5 -amino-2-thiazolecarboxylate, and the following IIa (substituents given): 3-Me; 3,5-di-Me; 3-Cl; N-Ac, 3-Cl; 3-Br; 3,5-di-Br; 3-I; 3-O2N; N-Ac, 3-H2N (III); 3-HO2C; 2-Me; 2,6-di-Ph; 2-Cl; 2-Br; 2-I; N-Ac, 2-I; 2-H2N; 2-HO; 2-HS; 2-HO2C; N,N-di-Me; N-Bu; N-n-hexyl (IV); N-PhCH2; N-benzal; N-Ac; N-Bz; N-ClCH2CO; N-Cl2CHCO; N-EtO2C; N-H2NC(:O); N-H2NC(:S) (V); N-H2N; N-Me, N-ON. The syntheses of III, IV, 5, 5'-**dinitrodiphenic** acid, and of **esters** of I are described. Some of these **esters** showed activity on Youmans medium but not on the protein-contg. Beewkes medium. V m. above 330.degree..

L18 ANSWER 6 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1949:10892 CAPLUS
DN 43:10892
OREF 43:2189g-i,2190a-c
TI p-Aminosalicylic acid
AU Justoni, R.; Terruzzi, M.; Pirola, C.
SO Farm. sci. e tec. (Pavia) (1948), 3, 509-25
DT Journal
LA Unavailable
AB cf. C.A. 42, 7273c. The following steps were investigated to find the most practical method of manuf. 2,4-H2N(O2N)C6H3Me is acetylated with Ac2O giving 95% of the Ac compd. which, treated with KMnO4 in MgSO4 soln at 95.degree., gives 90% p-nitro-.omicron.-acetamidobenzoic acid, m. 215.degree., 225 g. of which, refluxed with HCl or H2SO4 in H2O, gives 180 g. 2,4-H2N(O2N)C6H3CO2H. Replacement of the NH2 with OH through the diazo compd. involves considerable loss by decarboxylation, which cannot be avoided by changing either concn., temp., or pH. Dinitrophenylacetic acid, m. 180.degree., is prepd. by treating 135 parts PhCH2CO2H with a mixt. of 1300 parts H2SO4 and 350 parts KNO3 below 60.degree.. The Me **ester** is prepd. from 180 parts acid with HCl in MeOH or, better, by adding H2SO4 contg. 20% SO3 in MeOH and partially evapg. in vacuo after 24 hrs. standing. Part of the **ester** crystallizes directly, part is obtained from the filtrate by adding NaOAc and evapn.; total yield 160 parts. The **ester** treated with iso-AmNO2 and iso-AmONa (Borsche,

C.A. 6, 2422) forms 90% Me 6-nitro-3-indoxazenecarboxylate, and is then transformed into the nitrile (95%) of p-nitrosalicylic acid (I) by treating with NaOH. Sapon. with HCl gives 75, with H2SO4 83% I, purified through the Ba salt. The oxidation of 2,4-Cl(O2N)C6H3Me (II) to p - nitro - .omicron. - chlorobenzoic acid (III), m. 141-2.degree., is effected by adding a paste of II with (NH4)2Cr2O7 to H2SO4 at a temp. below 35.degree., heating finally to 55.degree., and mixing with ice; yield 63%. Oxidation of II with HNO3 gives 75% III. III is also prepd. in 75% yield from 2,4-H2N(O2N)C6H3CO2H through the diazo compd. 2,4-Cl(O2N)C6H3CN is prepd. in 50% yield from 2,4-Cl(O2N)C6H3NH2, through the diazo compd., with K2Ni(CN)4. Sapon. gives 80% III. I is prepd. from III with Ca(OH)2 and Cu salt or, better, with Ba(OH)2, but always with concomitant formation of 5,5'-**dinitrodiphenic** acid.
Hydrolysis of III with p-MeC6H4SO3Na, CuOAc, and MgO at 170.degree. under pressure for 10 hrs. gives 76-7% I. I is reduced with Raney Ni at 70-80 atm. H pressure and 40.degree. in 66-72% yield, or as the Na salt in 10% aq. soln. at a pH 8 at 20 atm. 4 hrs. in 90% yield. By heating m-aminophenol 218 dissolved in KOH 112 and H2O 350 and mixed with K2CO3 690 in H2O 450 parts at 90.degree. under atm. CO2 pressure, 180 parts p-aminosalicylic acid is obtained.

L18 ANSWER 7 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1946:29241 CAPLUS
DN 40:29241
OREF 40:5701f-i,5702a-g
TI Stereoisomeric salts of leucine Me esters
AU Weil, K.; Kuhn, Werner
CS Univ. Basel
SO Helvetica Chimica Acta (1946), 29, 784-96
CODEN: HCACAV; ISSN: 0018-019X
DT Journal
LA German
AB cf. C.A. 40, 2170.5. In order to detect small amts. of d(-)-leucine Me **ester** (I) in mixt. with large amts. of l(+)-leucine Me **ester** (II), the mixt. is converted into the salts of 2,2'-dihydroxy(1,1'-binaphthalene)-3,3'-dicarboxylic acid (III), of which the salt of I is only very slightly sol. (cf. loc. cit.). In lieu of III, other optically active acids may be used as long as I and II give diastereomeric salts of sufficiently different properties. It is also found to be advantageous to remove the main portion of II first and this may be achieved even with an inactive acid as long as the acid gives enantiomorphous salts (IV), i.e. not racemate crystals, with I and II. In this case the salts of II sep. until a 1:1 mixt. of I and II is reached. For this purpose, the properties, particularly the soly. of diastereomeric salts of I and II with optically active and inactive acids, are studied. II, b3 47.degree., b5 58.degree., b12 80.degree., is prepd. by **esterification** of l-leucine, [.alpha.]D20 -10.degree. (c 2.27, H2O), with MeOH-HCl, and decompn. of the **ester**-HCl, m. 147.degree. (cor.), with K2CO3. II has d413 0.9575, nD13 1.4327, d415 0.9555, nD15 1.4319, d417 0.9533, d418 0.9524, nD18 1.4307, d420 0.9504, nD20, 1.4299, d423 0.9465, d425 0.9452, nD20 1.4279, d428 0.9421, nD28 1.4267, nD30 1.4259, nD40 1.4218, [.alpha.]D17 16.5.degree., [.alpha.]D23 15.3.degree.. It is found that a racemic mixt. (V) of I and II in MeOH and in ether is completely dissocd. into I and II. In many cases it can be concluded from the soly. whether or not stable IV are formed. IV are with certainty present as solid ppts. in solvents in which no electrolytic dissocn. occurs when the soly. of IV is smaller than twice the soly. of I and II per se. If the soly. of IV in such solvents is equal to twice the soly. of I and II, then it may be concluded that the insol. ppt. consists of a mixt. of IV if the optically inactive component of the salt is monovalent, and dimerization of salt mols. in soln. can be considered to be impossible. The following salts are prepd.: II picrate, m. 136-7.degree., soly. in benzene at 29.1-9.5.degree., 0.13% .+-. 0.02%; picrate of V, m. 126.degree., soly., 0.15% .+-. 0.01%; acid oxalate of II, m. 180.degree., [.alpha.]D28 21.5.degree. (c 0.5, MeOH), soly. in MeOH at 15.degree., 2.2%, at 28.degree., 1.7%; acid oxalate of V, m. 169.degree., soly. in MeOH at 15.degree., 2.1%, at 28.degree., 1.5%; neutral oxalate of II, m. 161.degree., soly. in MeOH at 15.degree., 6.5%; neutral oxalate of V, m. 162.degree., soly. at 15.degree., 5.4%; 2,4-dinitrobenzoate of II, m. 143.degree., soly. in AcOEt at 28.5.degree., 2.5 %, and of V, m. 137.degree., soly., 2.4%; p-nitrobenzoate of II, m. 145.degree., soly. in AcOEt at 28.5.degree., 2.7%, and of V, m. 142.degree., soly. 3.2%; HCl salt (VI) of II, m. 147.degree. (cor.), [.alpha.]D26 20.85.degree. (c 4.47, MeOH), soly. at 16.9-17.4.degree. in ether, 0.12 g./l., in ether contg. 0.9 mol. HCl/l., 0.73 g./l., in ether contg. 2.76 mols. HCl/l., 2.1 g./l.; HCl salt of V, m. 113-14.degree. (cor.) [its soly. cannot be detd. because it is converted into racemic 2,

5-diisobutyl-3,6-diacipiperazine-HCl (VII); the free basic diketone liberated with the calcd. amt. of MeOK, m. 273.degree. (cor.)]. VII is not formed in MeOH soln. The active diketopiperazine (VIII), obtained from II, is formed only slowly in neutral or acid solns. VIII m. 263-4.degree. (cor.), [.alpha.]D25 -40.08.degree. (c 0.70, MeOH) (cf. Abderhalden and Funk, C.A. 2, 134). The formation of VII in an ether soln. contg. large amts. of VI and only a little racemic mixt. occurs very rapidly. When a mixt. of II and a small amt. of V is mixed with ether contg. HCl, VI crystallizes rapidly while the HCl salt of V is rapidly converted into VII and remains in soln. Citric acid and o-nitrobenzoic acid do not give cryst. salts with II. Succinic acid (IX) and II in AcOEt give a neutral salt, m. 85-8.degree. (cor.); IX and V give a neutral salt, m. 75.degree. (cor.). l(+)-Mandelic acid (X), m. 133.degree., [.alpha.]D26 163.degree. .+-. 1.degree. (c 1.3, H2O), and d(-)-mandelic acid (XI), m. 133.degree., [.alpha.]D -155.degree. .+-. 2.degree. (c 1.05, H2O), are prepd. by resolving dl-mandelic acid, m. 118.degree.. II-XI salt (XII), m. 105.degree., soly. in benzene at 29.3.degree., 0.95%; XII is assocd. in C6H6 to double mols.; II-X salt (XIII) m. 126.degree. (cor.), soly. 0.14%. Total racemate, consisting of V, X, and XI, m. 126.degree., soly. 0.14%. p-Methylmandelic acid and atrolactinic acid give well-crystd. salts in benzene with solubilities similar to those obtained from X and XI. II-d-tartrate m. 152.degree., soly. in MeOH at 15.3.degree., 10.35%. 6,6'-**Dinitrodiphenic** acid (XIV), m. 259.degree., is resolved with d- and l-MeCHPhNH2 into d-XIV, m. 229.degree. (cor.), [.alpha.]D25 135.degree. (c 1.5, MeOH), and l-XIV, m. 229.degree. (cor.), [.alpha.]D24 -134.degree. (c 1.6, MeOH). 2II-l-XIV (XV) m. 105-6.degree.; 2V-d-XIV m. 105-6.degree.; 2II-d-XIV and 2V-l-XIV give very sol. salts which are not obtained in a cryst. form. II and XIV in benzene give a salt, m. 162.degree., from which XIV is isolated with HCl, indicating that not XV but the still less sol. half-racemate of the compn. 2II-l-XIV.2II-d-XIV is formed. Similar results are obtained with V and d-XIV.

L18 ANSWER 8 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1941:13384 CAPLUS
DN 35:13384
OREF 35:2135g-i,2136a-b
TI Synthesis of certain local anesthetics of the biphenyl series
AU Case, Francis H.; Koft, Emil, Jr.
SO Journal of the American Chemical Society (1941), 63, 508-10
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA Unavailable
AB The acid chloride from 4,4'-O2NC6H4C6H4CO2H (by heating with PCl5 at 180.degree. and removing the POCl3) in PhMe and an excess of Et2NCH2CH2OH, refluxed 5 hrs., give .beta.-diethylaminoethyl 4-nitro-4'-biphenylcarboxylate, m. 52-3.degree.; HCl salt, m. 186-8.degree.; catalytic reduction in EtOH gives the 4-NH2 deriv. (I), m. 78-9.degree.. 5,5'-**Dinitrodiphenic** acid (II) is best prepd. by coupling diazotized 4,2-O2N(H2N)C6H3-CO2H in an ammoniacal soln. of Cu2O (16 g. from 28.5 g. NH2 acid); 2,4-I(NO2)C6H3CO2H is best prepd. by oxidation of 2,4-I(O2N)C6H3Me with KMnO4; the Me **ester** with Cu gives the Me **ester** of II. The acid chloride of II yields di(.beta.-diethylaminoethyl) 5,5'-dinitrodiphenate, m. 67-8.degree.; catalytic reduction gives the 5,5'-di-NH2 deriv. (II), m. 64-5.degree.. Details are given of the nitration of 42 g. of o-tolidine with KNO3 in a mixt. of 72 cc. of 15% oleum and 280 cc. concd. H2SO4 to give 37 g. of the di-NO2 deriv. and of the removal of the NH2 groups from 40 g. to yield 19 g. of [5,2-Me(O2N)C6H3]2; oxidation of 20 g. with CrO3 in AcOH (refluxing 10 hrs.) and reoxidation of the crude acid give 7.5 g. of 2,2'-dinitro-5,5'-biphenyldicarboxylic acid (IV), m. 327-8.degree. (decompn.); di-Me **ester**, m. 167-8.degree.; di(.beta.-diethylaminoethyl) **ester** of IV, a liquid; the monohydrate m. 80-1.degree.; the di-HCl salt m. 215-16.degree. (decompn.); attempted recrystn. from MeOH gives the di-Me **ester**, therefore catalytic reduction in EtOH was impracticable; Sn and HCl reduces 9 g. of the hydrate to 4 g. of di(.beta.-diethylaminoethyl) 2,2'-diamino-5,5'-biphenylcarboxylate (V), m. 91-2.degree.. Pharmacol. tests of I, III and V show that they have strong anesthetic power with varying degrees of toxicity (details will be published elsewhere).

L18 ANSWER 9 OF 9 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1940:4672 CAPLUS
DN 34:4672
OREF 34:745h-i,746a-f
TI Question of intramolecular asymmetric induction

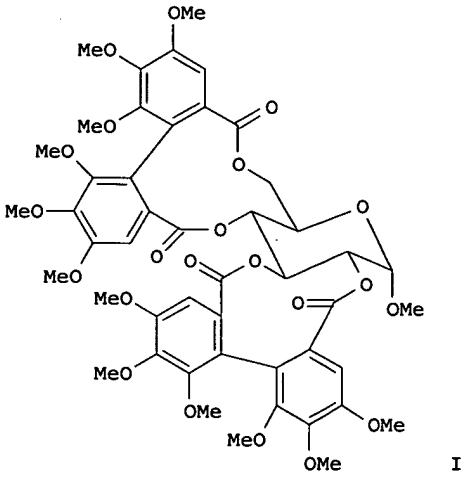
10082251

AU McKenzie, Alex.; Wood, Alex. D.
SO Journal of the Chemical Society, Abstracts (1939) 1536-44
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA Unavailable
AB Kuhn and Albrecht (C. A. 21, 2892) found that the quinine salt of 4,4'-**dinitrodiphenic** acid (I) results in 80% yield and that it is strongly d-rotatory, giving [.alpha.]5893 108.degree. in CHCl3, whereas quinine itself has [.alpha.]5893 -177.degree.; the salt was regarded as a homogeneous salt of the activated acid and when the quinine was eliminated from the salt, racemization was supposed to take place owing to the removal of groups which acted as obstacles to the free rotation of the C6H6 nuclei. From the following study it is seen that the **esters** were all l-rotatory in the solvents chosen and that there was no evidence that intramol. asym. induction of I had occurred under the directing influence of the optically active menthyl and bornyl groups. The conclusion is drawn that Kuhn's suggestion of "asym. rearrangement of the 1st order" with I under the influence of quinine must remain an open question in the meantime. I (10 g.) and (-)-menthol, heated at 130.degree. for 13 hrs., HCl being passed in at intervals, give 4 g. of the (-)-monomenthyl **ester** (II), amorphous, m. 166-7.degree., and a small quantity of the (-)-dimenthyl **ester** (III), amorphous, m. 61-2.degree.. On heating 27 hrs., 11 g. I gives 5.7 g. of II and 3.1 g. of III; III also results from the chloride of I or II and (-)-menthol. Values are given for [.alpha.]D20 and [.alpha.]546120: I -55.8.degree., -63.degree. (EtOH, c 1.04); -58.4.degree., -64.3.degree. (CHCl3, c 0.6768); -59.4.degree., -65.2.degree. (C6H6, c 0.598). II-, -89.8.degree. (EtOH, c 0.8964); -74.degree., -(EtOH, c 0.5676); -78.3.degree., -95.4.degree. (CHCl3, c 0.734); -83.6.degree., -96.3.degree. (C6H6, c 0.8668). (-)-Menthyl m-nitrobenzoate, -81.3.degree., -95.2.degree. (EtOH, c 1.4024); -83.7.degree. -99.2.degree. (CHCl3, c 1.5224); -86.7.degree., -101.4.degree. (C6H6, c 2.0815). (-)-Dimenthyl phthalate, -96.9.degree., -119.0.degree. (EtOH, c 0.5212); -95.4.degree., -113.8.degree. (CHCl3, c 1.6032); -95.9.degree., -(C6H6, c 1.9815). I (16 g.) and (-)-borneol, heated 18 hrs. at 165-75.degree., give 10.9 g. of (-)-dibornyl **ester** (IV), m. 201-2.degree., -40.degree., -48.1.degree. (Me2-CO, c 1.434); -46.9.degree. -56.3.degree. (EtOH, c 0.2132); -41.5.degree., -48.degree. (CHCl3, c 1); -32.8.degree., -41.3.degree. (C6H6, 0.533). Partial sapon. of IV with KOH in aq. EtOH gives (-)-monobornyl **ester** (V), amorphous, m. 178-9.degree., -28.9.degree. -33.8.degree. (CHCl3, c 2.1292); -25.degree., -29.6.degree. (C6H6, c 1.62). (-)-Bornyl m-nitrobenzoate, m. 76-7.degree., -36.4.degree., -43.2.degree. (EtOH, c 0.7284); -36.9.degree., -42.5.degree. (CHCl3, c 1.2475); -32.7.degree., -(C6H6, c 2.0045). (-)-Dibornyl phthalate, m. 104-5.degree., -82.9.degree., -97.1.degree. (EtOH, c 0.4582); -67.8.degree., -80.8.degree. (CHCl3, c 2); -64.5.degree., -(C6H6, c 2.1695). I and cinchonine in EtOH, heated 1 hr., give the cinchonidine salt, m. 220-1.degree., [.alpha.]546120 -185.6.degree. (CHCl3, c 4.025). The quinidine salt of I has [.alpha.]D20.5 -87.degree. (CHCl3, c 2.1325). The acid quinine salt of I m. 195-6.degree., [.alpha.]D20.7 46.6.degree., [.alpha.]546120 55.5.degree. (EtOH-CHCl3, c 1.0185); there is no evidence of mutarotation in 10 days. I (8 g.) and 18.4 g. of quinine in 360 cc. EtOH give 21.6 g. of a salt, m. 229-31.degree. (decompn.), [.alpha.]D21 102.4.degree., [.alpha.]546121 119.6.degree. (CHCl3, c 1.998); crystn. 3 times from C6H6 gives [.alpha.]D20 85.2.degree. (CHCl3, c 2.001); the mother liquor gives 1.5 g. of a salt m. 226-7.degree., (decompn.), [.alpha.]D20 108.5.degree., [.alpha.]546120 128.5.degree. (CHCl3, c 2.0084); on recrystn. from C6H6-CHCl3 the salt seps. with 2 moles of C6H6; the rotation of the dried salt is [.alpha.]D20 101.degree. (CHCl3, c 3.02). V with SOCl2 gives the acid chloride, m. 48-9.degree.; with (+)-borneol there results (+)-bornyl(-)-bornyl 4,4'-dinitrodiphenate, m. 212-13.degree.; the dl-dibornyl **ester** of I m. 200-1.degree..

10082251

=> d l2 bib abs 1-3

L2 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1996:290258 CAPLUS
DN 124:343841
TI Synthesis of Trideca-O-methyl-.alpha.-Pedunculagin. Diastereo-Favoritism Studies on Intramolecular Ester-Cyclization of Axially **Chiral** Biphenic Acids with Carbohydrate Core
AU Itoh, Toshiyuki; Chika, Jun-ichi; Shirakami, Shohei; Ito, Hideyuki; Yoshida, Takashi; Kubo, Yuki; Uenishi, Jun-ichi
CS Faculty of Education, Okayama University of Science, Okayama, 700, Japan
SO Journal of Organic Chemistry (1996), 61(11), 3700-3705
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
OS CASREACT 124:343841
GI



I

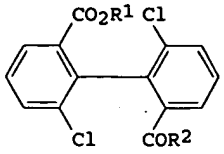
AB Total synthesis of trideca-O-methyl-.alpha.-pedunculagin I was achieved by a simple sequence. The key step is the synthesis of Me 4,6-O-benzylidene-2,3-O-[(S)-4,4',5,5',6,6'-hexamethoxydiphenoyl]-.alpha.-D-glucopyranoside through **ester** cyclocondensation of racemic hexamethoxydiphenoyl chloride with Me 4,6-O-benzylidene-.alpha.-D-glucopyranoside at the 2,3-position. The diastereoselectivity results obtained in the intramol. cyclization of hexamethoxydiphenic acid to the carbohydrate core raises a very interesting point in considering the pathway of (R)-**diphenic** acid biosynthesis.

L2 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1990:405950 CAPLUS
DN 113:5950
TI Preparation of optically active 6,6'-dichlorodiphenic acid half esters or halides
IN Saeki, Seitaro; Nishio, Yukiko; Sakai, Kiyoshi
PA Mitsubishi Kasei Corp., Japan
SO Jpn. Kokai Tokkyo Koho, 5 pp.
CODEN: JKXXAF
DT Patent
LA Japanese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 01299259	A2	19891204	JP 1988-129628	19880527
PRAI	JP 1988-129628		19880527		

OS MARPAT 113:5950
GI

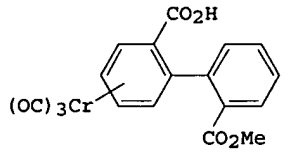
10082251



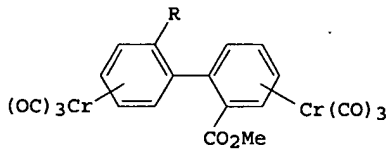
I

AB The title compds. (I; R1 = C1-4 alkyl; R2 = OH, halo) are prepd. as reagents for 1H-NMR detn. of optical purity of **chiral** alcs. and amines. Thus, redn. of 3-chloro-2-nitrobenzoic acid with NaBH4 in MeOH in the presence of NiCl2.6H2O gave 2-amino-3-chlorobenzoic acid which was diazotized with NaNO2 in aq. HCl and then coupled in the presence of aq. CuSO4 to give a **diphenic** acid I (R1 = H, R2 = OH). Esterification of the latter with (MeO)2SO2 in refluxing Me2CO in the presence of K2CO3 followed by partial sapon. in refluxing MeOH in the presence of aq. NaOH gave a half **ester** I (R1 = Me, R2 = OH) which was refluxed with SOCl2 to give I (R1 = Me, R2 = Cl).

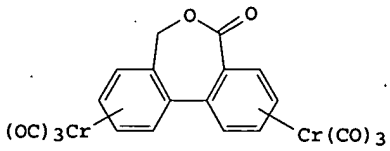
L2 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1981:102706 CAPLUS
DN 94:102706
TI Stereochemistry of metallocenes. XLVI. Biphenyl(tricarbonylchromium) complexes. V. Optically active tricarbonylchromium complexes of diphenic acid and its derivatives - enantiomeric purity, circular dichroism and absolute configuration
AU Schloegl, Karl; Schoelm, Richard
CS Inst. Org. Chem., Univ. Wien, Vienna, A-1090, Austria
SO Liebigs Annalen der Chemie (1980), (11), 1877-88
CODEN: LACHDL; ISSN: 0170-2041
DT Journal
LA German
GI



I



II



III

AB Title complexes of **diphenic** acid and its mono-Me **ester** [e.g., (+)-I and (-)-II (R = CO2H)] were prepd. by resoln. via their cinchonidinium salts, with enantiomeric purities .ltoreq.8%. Kinetic resoln. of II (R = CHO) via redn. with a **chiral** LiAlH4 complex was more successful (optical yield 33%). The products were (+)-II (R = CHO), alc. (-)-II (R = CH2OH) and lactone (-)-III. The chirality of the complexes was assigned by comparing their CD spectra with those of benchrotrenes of known abs. configuration.

=> d his

(FILE 'HOME' ENTERED AT 18:31:39 ON 22 JUL 2003)

FILE 'CAPLUS' ENTERED AT 18:31:49 ON 22 JUL 2003
L1 202 S DIPHENIC (P) (ESTER OR MONOESTER)
L2 3 S L1 AND CHIRAL
L3 0 S L2 AND BIARYL

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(FILE 'HOME' ENTERED AT 18:31:39 ON 22 JUL 2003)

FILE 'CAPLUS' ENTERED AT 18:31:49 ON 22 JUL 2003
L1 202 S DIPHENIC (P) (ESTER OR MONOESTER)
L2 3 S L1 AND CHIRAL
L3 0 S L2 AND BIARYL

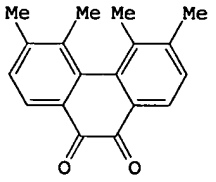
=> s l1 and achiral
4083 ACHIRAL
L4 0 L1 AND ACHIRAL

=> s l1 and cd
226282 CD
L5 5 L1 AND CD

=> s l5 not l2
L6 4 L5 NOT L2

=> d 1-4 bib abs

L6 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1993:494884 CAPLUS
DN 119:94884
TI Helical phenanthrenes. Part 4. Absolute helicities of twisted 9,10-phenanthrenequinones. Circular dichroism and chemical correlation to biphenyls
AU Fritsch, Rainer; Hartmann, Erwin; Brandl, Gert; Mannschreck, Albrecht
CS Inst. Org. Chem., Univ. Regensburg, Regensburg, D-8400, Germany
SO Tetrahedron: Asymmetry (1993), 4(3), 433-55
CODEN: TASYE3; ISSN: 0957-4166
DT Journal
LA English
GI



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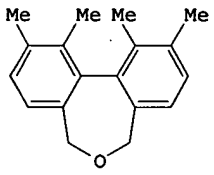
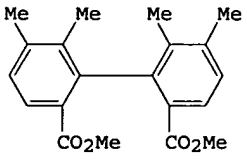


II



III

AB The abs. configuration of the nonplanar 9,10-phenanthrenequinone (-)546-I was detd. to be (M) by a four-step chem. correlation to the bridged biphenyl (-)365-II, the (M) helicity of which was proven via the CD of the conjugation band. The last step of the correlation consisted of the acyloin condensation of the **diphenic ester** (-)365-(M)-III, during which partial loss of optical purity was obsd. An intermediate 9,10-bis(trimethylsiloxy)phenanthrene is thought to racemize at a moderate rate, thereby causing some loss of activity. The relative configurations of twisted 9,10-phenanthrenequinones can be detd. by a series of weak Cotton effects between ca. 370 and 500 nm. These are neg. for (M) quinones, as shown by the above mentioned correlation to a bridged biphenyl. Liq. chromatog. on optically active sorbents served for most of the semipreparative sepns. of enantiomers and detns. of enantiomeric purity.

L6 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1966:26977 CAPLUS
DN 64:26977
OREF 64:4918c-d
TI Thermodynamics of ion association. XII. EGTA complexes with divalent metal ions
AU Boyd, S.; Bryson, A.; Nancollas, G. H.; Torrance, K.

10082251

CS Univ. Glasgow, UK
SO Journal of the Chemical Society, Abstracts (1965), (Dec.), 7353-8
CODEN: JCSAAZ; ISSN: 0590-9791
DT Journal
LA English
AB cf. CA 60, 6271f. Equil. consts. for the dissocn. reactions H2L2-
.dblharw. H+ and HL3- and HL3- .dblharw. H+ + L4-, where H4L represents
di(2-aminoethoxy)ethanetetraacetic acid (EGTA) have been detd. by a
potentiometric method at 5, 15, 25, and 35.degree., and at an ionic
strength of 0.1M. Calorimetric measurements have been made of the heats
of formation of 1:1 complexes of EGTA with the metal ions, Mg2+, Ca2+,
Sr2+, Ba2+, Zn2+, and Cd2+, and the data have been combined with known
stability consts. to give the corresponding entropy changes. The
thermodynamic functions for the formation of the alk. earth complexes are
discussed and compared with similar data for other aminocarboxylate
complexes.

L6 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1958:11058 CAPLUS
DN 52:11058
OREF 52:1979e-i,1980a-d
TI Natural plant substances with a nitro group. II. Constitution of
aristolochic acid II
AU Pailer, M.; Schleppnik, A.
CS Univ. Vienna
SO Monatshefte fuer Chemie (1957), 88, 367-87
CODEN: MOCMB7; ISSN: 0026-9247
DT Journal
LA Unavailable
AB cf. C.A. 51, 1125c. A substance similar to the aristolochic acid (I)
previously reported was found in the NaHCO3-sol. portion of the alc. ext.
from defatted roots of Aristolochia clematitis. This so-called
"noraristolochic acid" was designated aristolochic acid II (II) and
identified as 3,4-methylenedioxy-10-nitro-1-phenanthrenecarboxylic acid.
The brown crude acid (30 g.) was concd. to contain chiefly I and II by
extg. with Et2O, evapg. to dryness, taking up the residue in CHCl3, extg.
the acids with NaHCO3 soln., acidifying the filtrate with HCl, dissolving
the 6.2 g. brown flakes in H2O contg. NaOH, pptg. the K salts with KCl,
dissolving the salts in H2O, and acidifying to give 3.757 g. yellow acid
mixt. (III). III (1.078 g.) with CH2N2 gave 1.05 g. Me esters. The ester
mixt. (1.24 g.) dissolved in CHCl3 and the components sepd. by
chromatography in an Al2O3 column gave 422 mg. yellow II Me ester (IV), m.
274.degree., and 216 mg. yellow I Me ester (V), m. 284-6.degree..
Ultraviolet spectra showed max. for IV at 252 m.mu. (log .epsilon. 4.64),
298(4.22), and 358(3.76), and for V at 251 (4.35), 320(4.50), and
390(3.81). IV (104 mg.) sapond. with alc. KOH and acidified yielded 6 mg.
yellow II, m. 269-71.degree. (decompn.), .lambda. 251 m.mu. (log .epsilon.
4.51), 297 (4.15), and 353(3.65). Hydrogenation of IV with Pd-C in
glacial AcOH gave yellow 3,4-methylenedioxy-10-amino-1-
phenanthrenecarboxylic acid lactim, C16H9O3N, m. 304-6.degree., .lambda.
265 m.mu. (log .epsilon. 4.36), 276(4.45), 287(4.42), 327(3.88),
336(3.87), 340(3.86), 374(3.78), and 391(3.79). Hydrogenation of IV in
alc. with Pd-C gave a soln. with the spectrum of the lactam, .lambda. 265
m.mu., 278, 286, 327, and 340, and slight displacements at 370 and 387.
IV was dealkylated in resorcinol with HCl in a bomb tube (3 hrs. at
150.degree.) to 2,3-dihydroxy-10-nitro-1-phenanthrenecarboxylic acid, not
isolated, but oxidized with alk. KMnO4 to .omicron.-C6H4(CO)2O. Oxidative
decompn. of 250 mg. IV in alk. tetrahydrofuran with H2O2, methylation of
the product with CH2N2, and chromatography of the ester mixt. gave 70 mg.
tri-Me 5,6-methylenedioxy-2,2',3-biphenyltricarboxylate, m. 144-6.degree.,
b0.005 130.degree., sapond. with MeOH-KOH to the corresponding acid, m.
176-84.degree.. Decarboxylation of 1 g. III with Cu in quinoline and
chromatographic sepn. gave 270 mg. 3,4-methylenedioxy-10-nitrophenanthrene
(VI), yellow crystals, m. 174.degree., .lambda. 285 m.mu. (log .epsilon.
4.107) and 390(3.67), and 226 mg. yellow decarboxylated I,
3,4-methylenedioxy-8-methoxy-10-nitrophenanthrene, m. 212.degree.,
.lambda. 297 m.mu. (log .epsilon. 4.04) and 370(3.59). Decarboxylation of
II also gave VI. VI was hydrogenated in glacial AcOH with Pd-C to the
amine, 3,4-methylenedioxy-10-aminophenanthrene, which could not be
isolated but was acetylated with Ac2O to 3,4-methylenedioxy-10-
(diacetylamino)phenanthrene, m. 276.degree., also obtained from VI with Zn
dust in Ac2O in the presence of NaOAc. VI (200 mg.) with H2O2 in alk.
tetrahydrofuran gave 60 mg. 5,6-methylenedioxy-2,2'-biphenyldicarboxylic
acid (VII), m. 255-62.degree., not identical with the synthetic
4,5-methylenedioxy isomer (VIII). VII in MeOH with CH2N2 in excess Et2O
gave VII di-Me ester, m. 106-9.degree., b0.001 100.degree., not identical
with VIII di-Me ester. Dealkylation of 6 mg. VII with HCl and resorcinol
in a bomb tube gave 2 mg. 3,4-benzo-8-hydroxycoumarin (IX), m.

180-1.degree., .lambda. 225 m.mu. (log .epsilon. 3.58), 242(3.27), 268(3.16), 278(3.14), and 312(2.72). 2,3-Methylenedioxy-9-phenanthrenecarboxylic acid in glacial AcOH with Na2Cr2O7 on a steam bath yielded 42% red 2,3-methylenedioxy-9,10-phenanthrenequinone (X), m. 253-4.degree., characterized with .omicron.-C6H4(NH2)2 as its quinoxaline, m. 261-3.degree.. X (200 mg.) treated with alk. H2O2 in boiling 50:20 MeOH-tetrahydrofuran and the product acidified with HCl yielded 229 mg. VIII, m. 260-4.degree., methylated with CH2N2 in MeOH to the di-Me ester, m. 46-9.degree. b0.001 100-10.degree.. Similarly, 3,4-dimethoxy-9-phenanthrenecarboxylic acid was oxidized to 36% 3,4-di-methoxy-9-10-phenanthrenequinone, m. 180.degree. (quinoxaline, m. 214.degree.); the quinone (600 mg.) was oxidized to 620 mg. 5,6-dimethoxy-2,2'-biphenyldicarboxylic acid (XI), m. 207-8.degree.. XI heated with concd. HCl 4 hrs. at 150.degree. in a bomb tube gave 79% IX, m. 180-1.degree.; Me ether, m. 168-9.degree..

L6 ANSWER 4 OF 4 CAPLUS COPYRIGHT 2003 ACS on STN
AN 1957:5407 CAPLUS
DN 51:5407
OREF 51:1125c-i
TI Natural plant substances with a nitro group. I. The constitution of aristolochic acid
AU Pailer, M.; Belohlav, L.; Simonitsch, E.
CS Univ. Vienna
SO Monatsh. (1956), 87, 249-68
DT Journal
LA Unavailable
AB cf. C.A. 50, 10110b. Aristolochic acid (I), C17H11O7N, was identified as 3,4-methylenedioxy-8-methoxy-10-nitro-1-phenanthrenecarboxylic acid. I was isolated from the dried root powder of Aristolochia clematitis by degreasing with petr. ether, extg. with EtOH, evapg. the alc. in vacuo, treating the residue with dil. soda soln. and ether, after sepg. the ether soln. acidifying the soda soln. with HCl to form a brown ppt., boiling the crude acid ppt. under reflux 3 times with a little alc., digesting repeatedly with dil. KHCO3 soln. until no more dissolves, acidifying these solns. individually, combining the ppts. from all but the first, and recrystg. from HCONMe2-alc. (1:6) to cryst. I, dried at 140.degree. in vacuo, m. 281-6.degree. (decompn.). I was esterified with CH2N2 in dioxane to its Me ester (II), m. 281.degree., and decarboxylated with Cu powder in quinoline to 74% compd. (III), C16H11O5N, m. 212.degree. (3,4-methylenedioxy-8-methoxy-10-nitrophenanthrene). Hydrogenation of both I and II in AcOH with a Pt catalyst gave a compd., C17H11O4N, m. 319.degree. (3,4-methylenedioxy-8-methoxy-10-amino-1-phenanthrenecarboxylic acid lactam). Hydrogenation of III in alc. with Pd-C as catalyst yielded a compd., C16H13O3N, m. 170.degree. (3,4-methylenedioxy-8-methoxy-10-aminophenanthrene); in Ac2O with NaOAc and Zn dust, III yielded a compd. (IV), C18H15O4N, m. 274.degree. (3,4-methylenedioxy-8-methoxy-10-acetamidophenanthrene). Zinc dust distn. of I gave phenanthrene. Oxidative destruction of II in alk. tetrahydrofuran with H2O2 yielded a compd. (V). C16H12O7, m. 243.degree. (5,6-methylenedioxy-3'-methoxy-2,2'-biphenyldicarboxylic acid), which on methylation with CH2N2 in MeOH gave the di-Me ester, m. 114.degree.. Ether splitting from V in resorcinol with concd. HCl in a bomb tube (3 hrs. at 130.degree.) yielded 65% of a compd. (VI), C13H8O4, m. 204.degree. (2,3,3'-trihydroxy-2'-biphenylcarboxylic acid lactone), which methylated with CH2N2 in MeOH gave the di-Me ether (VII), m. 198.degree.. VII was oxidized with excess KMnO4 at pH 8 to o-methoxyphthalic anhydride, m. 160.degree.. 1,5,6-Trimethoxy-10-phenanthrenecarboxylic acid in AcOH with Na2Cr2O7 gave 60% 1,5,6-trimethoxy-9,10-phenanthrenequinone, m. 167.degree., which decompd. in alk. MeOH soln. with H2O2 gave 3',5,6-trimethoxy-2,2'-biphenyldicarboxylic acid; this on treatment with concd. HCl in a bomb tube (3 hrs. at 130.degree.) gave a compd., which on admixt. with VI showed no m.p. depression. The di-Me ether of the synthetic lactone was identical with VII. Detn. of methoxyl groups was carried out in the app. of Elek (C.A. 33, 28452) by a modified method. Samples of 3-5 mg. dissolved in 0.3 ml. (EtCO)2O were treated after cooling with 2 ml. const.-boiling HI and 0.5 ml. HI of d. 1.96, and heated 45-60 min. under the usual conditions. Ultraviolet absorption spectra are included for III in EtOH (compared with 9-nitrophenanthrene) and IV in EtOH (compared with 9-acetamidophenanthrene) and infrared spectra for solid I in KBr and III and IV in Nujol. 44 references.